

Surface Water-Groundwater interactions in sand dune ponds located in Doñana National Park

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Doñana National Park***

Memoria de Tesis presentada por la Graduada Dña. Ana Fernández Ayuso para optar al grado de Doctor por la Universidad Pablo de Olavide.

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Universidad Pablo de Olavide

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Tesis Doctoral

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ABSTRACT

The understanding of the surface water-groundwater interactions in the Doñana sand-dune ponds has progressively upgraded since the study of this topic began more than three decades ago. Nevertheless, there was a lack of updated knowledge about the characterization and differentiation in the behavior of each of the ponds that make up this ecosystem. Moreover, some of these ponds had never been studied before from a hydrogeological point of view. In this PhD Thesis, it has been deepened in these aspects from a multimethod approach:

First of all, knowledge about the water functioning of the Santa Olalla pond has been greatly improved. This is crucial since it is the only water body of this kind that has water throughout the year. Moreover, there are a large number of species, mainly birds, which are dependent on this condition. To achieve this objective, a wide spectrum of methodologies has been used, from more purely hydrodynamic methods (such as hydraulic gradients or water balances over multiple periods) to hydrochemical methods that include isotope analysis. Finally, time series analysis has also been performed to be able to reveal, mainly on an hourly time step, patterns not easily distinguished with the aforementioned methods. Through these techniques it has been determined that: The Santa Olalla pond owes its permanent hydroperiod to the existence of an underground flux of both local and regional type. This condition makes the difference between this pond and the others found in the study area, which are temporary. On the other hand, it has been proven that the functioning of the Santa Olalla pond differs on a seasonal basis. In this sense, it has been found that there are some differences in the direction of the groundwater flux between dry and wet seasons. Furthermore, it has been demonstrated that the regional aquifer plays a more crucial role during the summer when the levels of the local aquifer are lower. On the other hand, evaporation from the surface water is a significant water output from the pond. Besides, through stable isotopes analysis in water samples taken from the pond, it has been shown that the evaporative signal is greater in the centre of the pond than on the shores. These results reinforce the hypothesis that local groundwater discharge through the shores.

The second of the achievements of this thesis is the estimation, using daily water balances and thermal methods, of the rates of discharge and recharge of groundwater to three of these ponds (Santa Olalla, Zahillo and Sopotón) and vice-versa. Previous information of these rates was practically negligible (especially in the study-cases of the Zahillo and Sopotón ponds). In addition, water balances in the three ponds during similar periods have allowed the comparison of the functioning among all of them. These could be divided into discharge ponds, typology shared by the Santa Olalla and Sopotón ponds, with an estimated average discharge rates of 2.3 and 1.8 mm / day, respectively, and recharge ponds, which would be the typology of the Zahillo pond, whose recharge rate was 0.1 mm / day, during the study period. This behaviour as recharge pond would be the result of a change in its natural typology.

Lastly, it has been investigated the effect that groundwater withdrawals in Matalascañas Coastal Resort have in these ecosystems. To carry out this purpose, all the methodologies used to achieve the two aforementioned objectives have also been used in this case. With them, the impact of the extraction in the coastal resort on the Zahillo pond, whose flood surface has been reduced to more than one-sixth of the original size, has been revealed. Both the water functioning as a recharge

pond and the hydrochemical analysis of major ions in which it has been shown that surface water has a lower salt content than groundwater has pointed in this direction. However, in the Santa Olalla pond, there has been no sign by any of the methodologies used during the time studied of an altered hydrological functioning as a result of groundwater extractions.

Keywords: Surface water-groundwater interactions, Doñana National Park, permanent and temporary ponds, hydrodynamics, water balances, hydrochemistry, thermal model, time series analysis, anthropogenic impact.

RESUMEN

El conocimiento de las relaciones aguas superficiales-aguas subterráneas en las lagunas peridunares de Doñana ha mejorado de forma progresiva desde que se inició su estudio hace más de tres décadas. No obstante, faltaba información actualizada sobre la caracterización y la diferenciación en el comportamiento de cada una de las lagunas que conforman este ecosistema. Este trabajo se justifica, además, dado que, ciertas de estas lagunas no habían sido antes estudiadas desde un punto de vista hidrogeológico. En esta Tesis Doctoral se ha profundizado en tres aspectos desde un enfoque multimetódico:

En primer lugar, se ha perfeccionado el conocimiento sobre el funcionamiento hídrico de la laguna de Santa Olalla. Esto tiene interés, ya que se trata del único cuerpo de agua de esta tipología que tiene agua durante todo el año y hay un gran número de especies, principalmente aves, que dependen de esta condición. Para la consecución de este objetivo, se han utilizado tanto métodos puramente hidrodinámicos, como la estimación de gradientes hidráulicos o la realización de balances hídricos en múltiples periodos de tiempo, como métodos hidroquímicos que incluyen análisis de isótopos. También se han realizado análisis de series temporales para poder identificar, principalmente a escala horaria, patrones no fácilmente detectables con los métodos anteriormente mencionados. Mediante estas técnicas se ha determinado que la laguna de Santa Olalla debe su hidroperiodo permanente a la existencia de una alimentación subterránea de tipo tanto local como regional. Esta condición marca la diferencia entre esta laguna y las demás en la zona de estudio, de hidroperiodo temporal. Por otro lado, se ha comprobado que el funcionamiento de la laguna de Santa Olalla difiere desde el punto de vista estacional. En este sentido, se ha constatado que existen inversiones de la dirección del flujo entre estaciones secas y húmedas y que el acuífero regional cobra más importancia durante el verano, cuando los niveles del acuífero local están más deprimidos. Por otro lado, la evaporación desde la lámina de agua juega un papel fundamental en las salidas desde la laguna. Además, a través del análisis de isótopos estables en muestras de agua tomadas de la laguna, se ha evidenciado que la señal evaporativa es mayor en el centro de la laguna que en las orillas. Estos resultados refuerzan la hipótesis de la descarga de agua subterránea local a través de las orillas.

El segundo de los logros de esta tesis es la estimación, mediante balances hídricos diarios y métodos térmicos, de las tasas de descarga y recarga de agua subterránea hacia tres de estas lagunas (Santa Olalla, Zahillo y Sopotón) y viceversa. La información previa sobre estas tasas era muy escasa, especialmente en el caso de las lagunas de Zahillo y Sopotón. Además, la realización de balances hídricos en las tres lagunas durante periodos de tiempo similares ha permitido la comparación del funcionamiento de cada una de las lagunas. Esto se ha podido identificar lagunas de descarga, tipología que comparten las lagunas de Santa Olalla y Sopotón, con tasas media de descarga estimada de 2.3 y 1.8 mm/día, respectivamente, y lagunas de recarga, que sería la tipología de la laguna de Zahillo, cuya tasa de recarga es de 0.1 mm/día en el periodo estudiado y que sería el resultado de un cambio en su tipología natural.

En último lugar, se ha investigado el efecto que tienen las extracciones de agua subterránea para consumo humano del núcleo costero de Matalascañas en estos ecosistemas. Para llevar esto a

cabo, se han utilizado también en este caso metodologías anteriormente mencionadas. A través de ellas se ha puesto de manifiesto la afección de la laguna de Zahillo, cuya superficie de inundación se ha reducido a más de la sexta parte de la cubeta original, como consecuencia de las extracciones en el mencionado núcleo costero. Tanto el funcionamiento hídrico como laguna de recarga como los análisis hidroquímicos de iones mayoritarios, en los que se ha comprobado que el agua superficial tiene menor contenido en sales que el agua subterránea, han apuntado en esta dirección. No obstante, en la laguna de Santa Olalla no se han observado indicios de un comportamiento hídrico alterado a consecuencia de las extracciones mediante ninguna de las metodologías utilizadas.

Palabras clave: Relaciones aguas superficiales-aguas subterráneas, Parque Nacional de Doñana, lagunas permanentes y temporales, hidrodinámica, balances hídricos, hidroquímica, modelo térmico, análisis de series temporales, impacto antrópico.

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¡Pájaro del agua!

Amo el son errante
y azul que desgranas
en las hojas verdes,
en la fuente blanca.

¡No te vayas tú,
corazón con alas!

Juan Ramón Jiménez

CHAPTER 1: Introduction



I. INTRODUCTION

I.1. Scope and structure of the thesis

Wetlands provide a large number of ecosystem services such as sediment and nutrient retention, reservoirs of biodiversity, cultural and heritage values or carbon sinks contributing to climate change mitigation. All of these services and more are listed by the RAMSAR Convention (De Groot *et al.* 2006). Despite of wetlands providing numerous services, there is a general trend to their loss. In the past century, 64% of the existing wetlands on the planet have been lost, at a rate three times greater than the forest loss. The main causes of their decline are (i) changes in land use and specifically the increase in the land use for both agricultural and grazing activities, (ii) climate change, (iii) and the rapid urbanization in coastal areas and river deltas (Xu *et al.* 2019).

There is a wide range of examples of wetland degradation caused by anthropic activities. In Spain, the recent case of Tablas de Daimiel National Park is well known. The wetland in this protected area was in danger as a consequence of the withdrawal of large amounts of groundwater for the irrigation of vineyards and herbaceous crops. An inversion of the hydraulic gradients took place due to the intensive exploitation of the groundwater resources. Therefore, the wetland changed from discharge type (receiving water from the aquifer) to recharge type (water from the wetlands infiltrated towards the aquifer). This circumstance caused Las Tablas de Daimiel to remain dry for three decades (1980 to 2010). Nowadays the levels have been recovered, although it still needs artificial water inputs during the driest periods. Another consequence derived from the lack of water was a decrease in the great biodiversity of birds that were found originally in this ecosystem (Llamas 2005; Martínez-Santos *et al.* 2018).

In other areas of the Mediterranean with a similar climate, other cases of wetlands depletion are common. Groundwater extractions for water supply or irrigation have had significant negative effects in protected wetlands such as Lake Koronia in Greece, Arzaq Oasis in Jordan, etc. On some occasions, the poor situation of such wetlands has been solved with the authorities' intervention (Green *et al.* 2017). At an international scale, deterioration in other RAMSAR systems has been documented, such as the dune ponds in Veracruz in Mexico as a consequence of incorrect management techniques (Peralta-Peláez *et al.* 2019).

The water use rights in Doñana Natural Area, one of the largest and most emblematic wetland in Europe (Green *et al.* 2016), is leading to disputes since the 1970s about the terms in which they have been managed. From those years onwards, the aquifer was intensively exploited for the irrigation of strawberry crops and fruit trees. The groundwater used for this purpose is taken from extensive areas adjacent to the National Park. The area designated under this protection status, along with the Natural Park area, shapes the Doñana Natural Area earlier mentioned. A decade later, the small coastal resort Matalascañas, whose water supply is solely satisfied with groundwater, started to grow (Suso and Llamas, 1993; Serrano and Serrano, 1996; Dimitriou *et al.* 2017). This increased the demand for water resources at the Doñana aquifer even more. Nowadays, the groundwater withdrawal for urban water supply is limited to 2.75 hm³ per year by the Guadalquivir River Basin Authority water concession. Nevertheless, it was disclosed to reach 3.25 hm³ per year when the groundwater began to be extracted for this use in 1990 (Dimitriou *et al.* 2017). Groundwater for this use is being withdrawal by five pumping wells, some of them located

at less than 1 km from the sand-dune ponds. Even though some authors (Hollis *et al.* 1989) have suggested their relocation further away from the ponds, to date, it has not been any measure implemented to soften this anthropic impact.

A correct study of wetlands requires an approach at multiple spatial and temporal scales. This comprises to deeply understand the surface water and groundwater interactions as well as to determine to what extent the various external agents (such as extractions, changes in land use or increase in temperatures) have an effect on the entire system.

The Guadalquivir River Basin Authority (DHG as for the Spanish acronym), the body responsible for water management in this area, often finds it difficult to meet the interests of the diverse stakeholders so that the natural state of the Doñana landscape and the dependent ecosystems are not endangered. In this context, in 2016, an agreement between the Guadalquivir River Basin Authority and the External Geodynamics Group of the Pablo de Olavide University was established, which aimed to study the relationships between surface water and groundwater in one of the key ecosystems of Doñana: the sand-dune ponds.

This PhD thesis is embedded within the framework of the mentioned agreement. There were gaps related to the knowledge of this systems that needed to be solved, mainly the lack of recent studies about surface water/groundwater in the studied ponds and the absence of continuous dataset of surface water level evolutions in the ponds to detect sub-daily patterns. The assessment of the hydrological functioning of three sand-dune ponds in Doñana national park is the central theme of the work. The presented research explores the surface water-groundwater interactions with the view of three complementary methods: hydrodynamics, thermal-hydrochemical and time series

analysis. As illustrated in Figure 1, each method is presented as a separate chapter and addresses particular Research Questions (RQ) which had lead this research. Chapters II, III and IV, include peer-reviewed chapters' books (Simposio del Agua en Andalucía) and research articles published in both national (Geogaceta) and international journals (Hydrological Sciences Journal, Water and Groundwater). Each of the articles has its discussion and conclusions sections. Accordingly, this thesis has been elaborated as a "compendium of articles" in compliance with the standards of the PhD Programme of the Pablo de Olavide University.

In Chapter II, first of all, daily water balances in Santa Olalla permanent pond, characterization of physical-chemical parameters from January 2015 to March 2016 and a comparison between the altitude of surface water level and shallow piezometers were done to address the RQ1. Hydraulic gradients were also calculated. Later on, once the sea tides were detected in medium - depth water tables close this permanent pond, hydraulic parameters in the area were estimated through tidal efficiency method and time lag method. Finally, in Santa Olalla, Sopetón and Zahíllo sand-dune ponds daily water balances during the same time period were developed to estimate discharge and recharge rates in the mentioned ponds, thus contributing to RQ2. Trends of water tables during the 2013-2016 years measured in piezometers close to dried out ponds and Santa Olalla permanent pond were also analyzed to address RQ3.

In Chapter III, the analysis of physical-chemical parameters in Santa Olalla pond perimeter resulted to be an optimal approach to assess RQ1. In addition, thermal methods worked with 1-D-temp pro were used to deal with RQ2 to contrast with the results obtained by water balances. On the other hand, major ions analysis, isotopes analysis and saturation indexes estimation of both surface water and groundwater reinforced the conceptual model of the sand dune ponds.

I. Introduction

Differences found among them were used to some extent to contribute to RQ3.

In Chapter IV, time series analysis on nine hydrometeorological datasets was carried out. Sensors used to record three-hourly data were installed in the surface water from Santa Olalla pond, and piezometers whose depth ranged from 2.7 to

100 m. Its analysis through Prophet and Wavelet techniques allowed at the same time the consecution of RQ1 and RQ3.

Finally, Chapter V, summarizes the findings of the individual chapters with regard to their implication to the research questions and the objectives followed in this thesis.

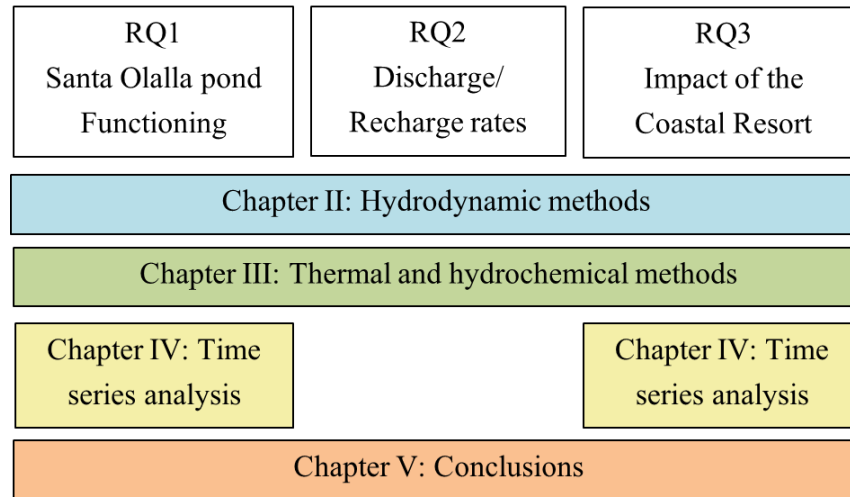


Figure 1: Outline of the thesis and relation of the chapters with the discussion of the RQ (Research Questions)

I.2. Objectives

I.2.1. General Objectives

The main goal of this doctoral thesis is to improve the knowledge about the hydrological functioning of Zahillo, Taraje, Sopetón and

Santa Olalla sand-dune ponds, located in the Doñana National Park. The lack of recent studies about the aforementioned ponds and the

absence of available water level evolution data at a sub-daily time step have motivated this target. Special emphasis has been set on the study of the Santa Olalla pond, as it is the only permanent pond and the largest in the area

I.2.2. Specific objectives

To reach a better understanding of the sand-dune ponds systems, three RQ have been formulated.

RQ1: Which is the hydrological functioning of Santa Olalla permanent dune-pond? Has it been modified across time? Which are the differences from the other sand-dune ponds?

RQ2: Which are the discharge/recharge rates in the main sand dune ponds in Doñana National Park?

RQ3: Is the coastal resort having an effect on the hydrological functioning of these sand-dune ponds? Have been any changes in ponds hydrodynamics/hydrochemistry across time?

From these, four specific objectives have been developed to address them:

SO1: Get insight about the surface water-groundwater interactions in the time

period June 2016- January 2018 via time series analysis of surface water and groundwater levels in piezometers of varying depth from 2.7 m to 100 m and a pumping well of 180 m deep (RQ1, RQ3). It will be addressed in Chapter IV.

SO2: Study the discharge-recharge rates in the mentioned ponds during the study period 2016-2018 through water balances and thermal methods that will be detailed in section 1.5 (RQ2). This objective will be addressed in Chapters II and III.

SO3: Characterize the hydrochemistry of the surface water, shallow groundwater and medium depth groundwater in the study site. This has been done by major ions and isotopes analysis and well as by saturation indexes estimation (RQ1, RQ3). It has been carried out in Chapter III, although there are also some results in Chapter II.

SO4: Analyze the impact of the groundwater extractions in the coastal resort of Matalascañas on the studied ponds (RQ3). The results concerning this objective are developed in Chapters II, III and IV.

I.3. Background

The importance and vulnerability of the Doñana ponds have led to a multitude of studies, doctoral thesis and scientific publications, mostly about its hydrological, ecological and biological aspects.

The first inventory of ponds was prepared by Bravo and Montes (1993). They identified 308 ponds greater than 100 m². The total number of ponds is highly variable, as it depends on the climatic conditions of each year. In a very wet year, more than 3,000 bodies of water have been distinguished (Green *et al.* 2107). There is also a rich morphological and typological diversity among the water bodies. The majority of the ponds receive water from the Doñana Aquifer (see section I.4.3). The morphological conditions of the area cause some ponds to be deeper than others, although the vast majority is not deeper than one meter.

Vela (1984) studied the hydrogeology and hydrogeochemistry of the ponds for the first time. A few years later Vela *et al.* (1991), modelled the possible damage to the ponds for a scenario in which the extractions at the coastal resort of Matalascañas reached a certain threshold (4 hm³ yr⁻¹). This was carried out via a two-dimensional modular flow model under the assumption that the aquifer was entirely unconfined.

Surface water-groundwater interactions started to be studied in detail in the works of Sacks (1989) and Sacks *et al.* (1992). In these contributions, a two-dimensional solute-transport flow model was developed in the Dulce-Santa Olalla-Pajas ponds system. The model revealed water recharge processes to the aquifer or, on the contrary, groundwater discharge from the aquifer to the pond in some areas. The processes depended on the season of the year as well as on the

classification of a year as “wet” (rainfall reached 15% higher values than the average) or “dry” (rainfall was 15% lower than the average) (Sacks, 1989). That is, the flow directions were modified according to these conditions. However, in terms of net balance, discharge to Santa Olalla pond was found to be the main process taking place.

Coleto (2003) added the study of ecological aspects (biogeochemical cycles, functional genetic classification, etc.) to the more purely hydrogeological knowledge, given the remarkable degree of dependence of the first on the latter. She also elaborated another pond inventory, in which she accounted for 680 of them with an area greater than 20 m², twice as large as listed in 1993. A total of 400 corresponded to the National Park and the rest to the Abalario area, in the Natural Park (see section 1.4.1).

The system of ponds located in the Doñana National Park was reviewed in Lozano (2004). She collected data and sampled water for isotopic analysis between 1998 and 2001. Moreover, she established a numerical model specially focused on the functioning of Dulce and Santa Olalla ponds. The model was carried out under the assumption that the sand aquifer was, in fact, a multi-layered groundwater body, simplified into an Upper Unit and a Lower Unit, separated by a clayey level that behaves as a confining layer. During the period under study, she was able to identify that the main water exchange between the ponds and the aquifer took place through the ponds’ shores and the first 10 m of the aquifer. The sub-superficial water flux from the Dulce pond to the Santa Olalla pond during the wet season was distinguished as well. Finally, the isotopic analysis and the numerical model also revealed that the evapotranspiration through vegetation was a crucial factor to be taken into account.

The research group headed by E. Custodio and M. Manzano from the Barcelona Polytechnic University and the Cartagena Polytechnic University has also contributed with extensive knowledge in the field of Doñana hydrogeology through the application of a wide range of methodologies: thermal methods, hydrochemical modeling in some areas of the aquifer, etc. Their work has led to the publication of numerous articles and books. Some of them are informative, such as Custodio *et al.* (2009), and others are more focused on the hydrogeological functioning in the Doñana system: Custodio (2010), Manzano *et al.* (2009, 2013).

Other authors provided relevant information about the ponds' status and their connection with groundwater from a more biological and ecological approach. Examples of this, are the numerous works of authors such as García-Murillo and Sousa (1997, 1999), Muñoz-Reinoso (1995, 1996, 2001a, 2001b), Muñoz-Reinoso and García-Novo (2000) and Sousa and García-Murillo (1998, 1999, 2003). These authors linked the change in vegetation seen around the pond with possible lower groundwater inputs to the ponds. Moreover, in Bustamante *et al.* (2005) and Diaz- Paniagua and Aragonés (2015), remote sensing techniques were used to reveal changes in the hydroperiod and flood surfaces of the sand-dune ponds. In the second-mentioned study, the impact of a Golf course, suspected of using groundwater resources which was opened in the Coastal

Resort in 2000 and closed in 2016 was claimed to intensify the desiccation trend of some of the ponds. Diaz-Paniagua (2015) has also coordinated a book describing this the biology and history of this unique ecosystem in detail.

Finally, Serrano and Serrano (1996) and Serrano *et al.* (2008) studied a shift in the dynamics of amphibian egg-laying. The authors attributed this circumstance to the modifications in the hydrological functioning of some of the ponds. The aforementioned author has also participated in the work of Dimitriou *et al.* (2017), in which a numerical model that relates the extractions in Matalascañas Coastal Resort with the current status of the ponds was carried out. These authors evinced that there was a decreasing trend of piezometric levels during the study period (1991-2013) which was not followed up by the same trend in precipitation events.

Other studies in which the effect of the groundwater withdrawal on the ponds was investigated were that of Rebollo (2007) and Rebollo *et al.* (2008). In such studies, spectral analysis and correlation techniques were applied to six time-series of hydraulic heads at a daily time-step. These studies revealed that effect of the groundwater withdrawal was clear in the area where the ponds are placed. Furthermore, the damage distinguished in the Charco del Toro pond area, which is currently dried out, was especially significant.

I.4. Study site

I.4.1. Geographical and institutional setting

The Doñana Natural Area is located in the southwest of Spain, in the coastal plain of the Gulf of Cádiz, between the Tinto River estuary and the Guadalquivir River mouth (Dimitriou *et al.* 2017). The Iberian Pyrite Belt, rich in iron sulphides, is located to the North. The maximum altitude in the Doñana area is 47 m asl and the minimum is the sea level, at the coastline. It has a great variety of ecosystems. They can be broadly divided into four types (Lozano 2007): mobile dunes, stabilized dunes, the marshes and the “Vera”, which is the contact area between the stabilized dunes and the marshes.

The mobile dune system is located in the southwest. It consists of four to eight dune fronts of aeolian sands advancing towards the marsh. The depressions between the dune trains are called “Corrales”, which have pine and shrub vegetation and are flooded after the first rainfall events of the year (Muñoz-Reinoso, 1996).

The sand-dune ponds are situated in the stabilized dune area. This ecosystem is located on the west of the Doñana National Park, between the mobile dunes and the “Vera” (Guardiola and Jackson, 2011). The typical native vegetation is the Mediterranean scrub (rosemary, cistus and lavender) and black bush vegetation, such as heather, in the most low-lying areas with high humidity. The vegetation found in the white bush ecosystem, in the drier areas, is formed by species such as rock rose (*cistus salvifolius*). One of the most frequent tree species found in this ecosystem is the stone pine (*pinus pinea*), which is an introduced species. Its high prevalence is the consequence of several reforestations, also of eucalyptus (*Eucalyptus Globulus*), especially in the 50s. The eucalyptus trees were removed later, as they were causing soil acidification and decreasing groundwater levels, but most stone pines remain, displacing native species

such as junipers (*Juniperus Macrocarda*), wild olive trees (*Olea Europea*

var. silvestris) and corkoaks (*Quercus suber*), which can be currently identified as secondary species in isolated areas (Finlayson *et al.* 2008).

The marsh is the most known landscape in Doñana since it spreads across more than half of its surface. Its appearance differs in great magnitude between winter and spring, when it is flooded, and the summer season, in which it dries out. Its importance as a wetland is extraordinary, given that more than 150 species of birds which nest, winter or simply pass by the marsh are recorded. Endangered bird species listed by the IUCN such as the iberian imperial eagle (*Aquila adalberti*) or the white-headed duck (*Oxyura leucocephala*) are easily seen in Doñana. Examples of aquatic birds in Doñana are the marbled teal (*Marmaronetta angustirostris*) and the locally extinct ferruginous duck (*Aythya nyroca*), the flamingo (*Phoenicopterus roseus*), the purple heron (*Ardea purpurea*), the glosst Ibis (*Plegadis falcinellus*) or the red-knobbed Coot (*Fulica critata*) (Seo Birdlife, 2019).

Finally, the “Vera”, is an area of great biological richness, as the groundwater discharge enables life for herbivores and birds when the marsh dries out (Muñoz-Reinoso, 2009). Endemic carnivorous animals such as the iberian lynx (*Lynx pardinus*), the most endangered feline in the world, can be found in this ecosystem. Other mammals such as deers and bucks have chosen the “Vera” as their habitat in Doñana.

The Doñana Natural Space consists on the ensemble of the Doñana National Park and the Doñana Natural Park. The first one was declared in 1969 and has 54,251 ha. distributed among the municipalities of Almonte, Aznalcázar, Hinojos and La Puebla del Río, in the provinces of Cádiz, Huelva and Seville. On the other hand, the Natural Park was established in 1989 to protect the adjacent areas of the National Park. Its area has progressively increased up to 68,236 ha.

covering fourteen municipalities: Almonte, Aznalcázar, Bollullos del Condado, Bonares, Hinojos, Isla Mayor, Lucena del Puerto, Moguer, Palos de la Frontera, Pilas, La Puebla del Río, Rociana del Condado, Sanlúcar de Barrameda, Villamanrique de La Condesa. All The management of the Doñana National Park is the responsibility of the Spanish government, whereas competences of the Natural Park are of the regional government of Andalusia (Palomo *et al.* 2014).of them belong to the provinces cited above, located in southwestern Spain.

Lastly, the Doñana Biological Reserve (Figure 2) occupies 6.794 ha. of the Doñana National Park. It belongs to the Doñana Biological Station, which is a research institute of the Spanish National Research Council (CSIC for its Spanish acronym). It was the first protected area in Doñana Area to be declared. This Reserve and the Guadiamar Biological Reserve have the highest level of conservation among the Doñana protected areas. Their use is restricted for scientific research and species conservation.

In addition, Doñana area also has international protection statuses which highlight its international importance. It is a UNESCO Biosphere Reserve (1980), a World Heritage Site by UNESCO (1994), a Special Area for Birds (ZEPA) (2003), a Special Area of Conservation (ZEC) (2012), it is on the Green List of the International Union for the Conservation of Nature (IUCN) (2015), a RAMSAR wetland (2005) and a Place of Community Interest (LIC) (2006).

The history of the Doñana area as a natural space dates back to 50s. At that time, the perception of the area formerly owned by the Duchess Doña Ana de Mendoza, of the family of the Dukes of Medina Sidonia, changed from being a plain hunting ground into a recreational area. People with artistic interests and naturalistic concerns became the driving force behind this change in paradigm. The area became popular for nature conservationists over the years and

culminated in the acquisition from the CSIC and World Wide Fund for Nature (WWF) of 6974 ha. in 1965 that would constitute de Doñana Biological Reserve and would mean the beginning of the natural space (Corona *et al.* 1988).

Nowadays, the economic activities permitted in the Doñana Natural Space are specified in the Master Plan for Use and Management (BOJA, Decreto 48, 2004). Currently, in the Natural Park, forest uses, hunting and fish farming, agriculture, aquaculture and extensive livestock are allowed. There is also tourist activity and religious pilgrimages around the Park. All these activities are subject to restrictions (Martín-Lopez *et al.* 2011).

In the National Park, activities authorized are extensive livestock, collection of pine cone, shellfish capture and beekeeping. The transit of vehicles is solely allowed for authorized people on the roads prepared for this use and at a limited speed. Tourism activities are very limited and permits are concentrated on a few companies. Finally, for religious pilgrimages throughout the year, the transit of people, vehicles and animals is permitted on certain paths (Oñate *et al.* 2003).

Water resources are the main precondition for socio-economic development, as well as for the maintenance of existing natural and environmental values (Palomo *et al.* 2011). The struggle over water use and rights among farmers, rice farmers and water managers has not yet been resolved sustainably. The actions taken by the Guadalquivir River Basin Authority comprise crop surfaces purchase and the closure of some of more than a thousand illegal wells via which water from the Doñana aquifer is withdrawn (Guadalquivir River Basin Authority, 2019). Moreover, a law which allows the transfer of 19.9 hm³ of water resources from the Tinto, Odiel and Piedras Basin Authority has been recently approved (BOE, Ley 10, 2018).

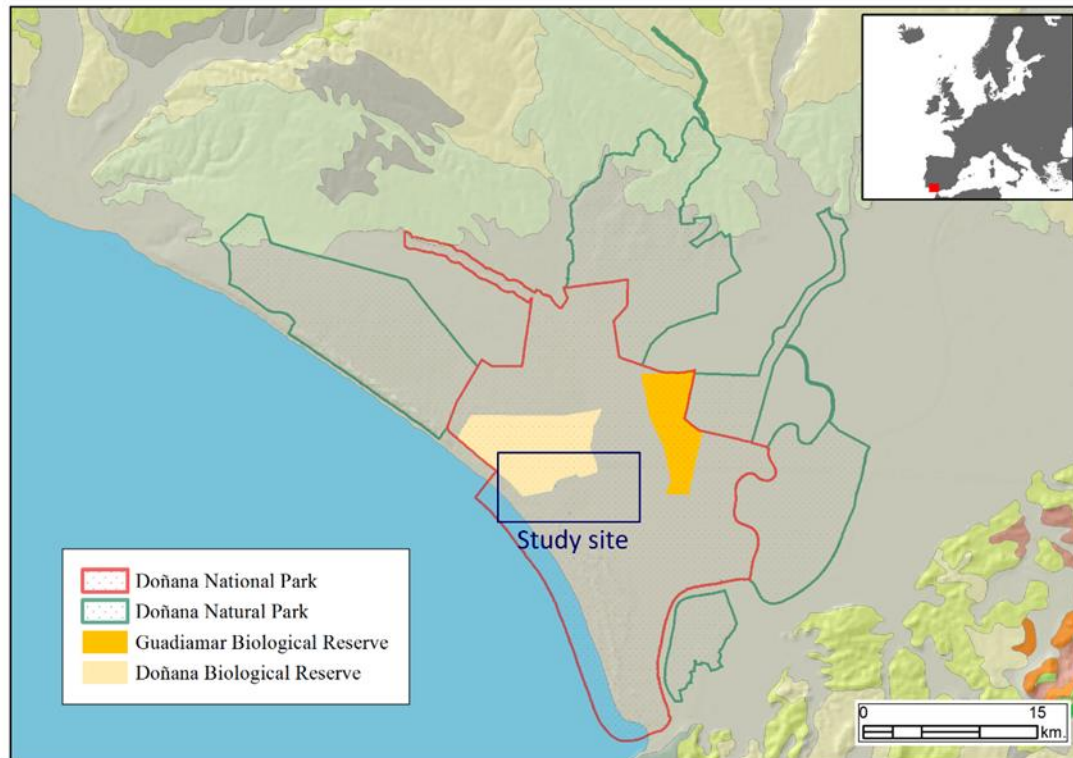


Figure 2: Main protected areas in the Doñana Natural Space.

Moreover, urban water use must also be considered, given that several populated areas, such as Matalascañas or El Rocío, are exclusively supplied by groundwater. Although the proportion of this water consumption is insignificant compared to the agricultural use, it is being withdrawn much closer to the ponds. This will become even more critical considering future increases in temperature (and thus evapotranspiration rates) as well as changes in the seasonal component normally associated to precipitations under a warming climate (Guardiola and Jackson 2011).

To address this topic there are some European rules whose objective is to protect groundwater resources of and wetlands. For instance, the Water Framework Directive (2000/60/CE) follow up requires a good quantitative status of groundwater bodies. Failure to comply with this condition in the Doñana area during the past years has led to complaints by the European Commission. Furthermore, there has also been a breach of the Habitats Directive (92/43/ECC) and the Bird Conservation Directive (2009/147/EC) since these wetlands provide habitat to numerous endangered birds.

I.4.2. Climatic setting

The climate of Doñana is of subhumid Mediterranean type with Atlantic influence (Manzano *et al.* 2013) and a marked seasonality. The summer months, generally from June to September are characterized as dry, with temperatures sometimes higher than 45°C. The pluviometric regime is very variable during the year, as well as interannually, although most of the precipitation events take place between October and April. The fewest part takes place from June to September. Most of the precipitation events occur during the fall. However, there are years in which relative and even absolute maximums during the spring occur (Custodio *et al.* 2009). This fact leads to the variability of the hydro-period of the wetlands each year, as the temporary ponds do not flood until the cumulative rainfall reaches more than 150 mm per year (Díaz-Paniagua *et al.* 2015).

The average precipitation inbetween 1978 and 2014 was 548 mm (Díaz-Paniagua *et al.* 2015) and in the years in which the data for this thesis were recorded (2015 to 2018) the average was 522 mm. The years 2015 and 2017 registered a cumulated rainfall below the average (400 mm per year) and the years 2016 and 2018 had values over the average (600 mm per year).

The prevailing winds in the area are of SW direction and average number of hours of insolation is 3,000 per year (Ramos-Fuertes, 2012). These conditions, together with the low altitude and the high temperatures, promote a high rate of evapotranspiration and supposes an entryway of marine aerosol to the system (with NaCl) (Montes *et al.* 1982). The potential evapotranspiration calculated by the Thornthwaite method is 840 mm/year, almost the double of the average annual precipitation (Ramos-Fuertes, 2012). The same authors obtained the value of 420 mm/year of actual evapotranspiration. Actual evaporation data obtained by a meteo-lysimeter installed in Doñana area with no vegetation ranged

between 0.4 and 0.6 mm/day (Kohfahl *et al.* 2019).

I.4.3. Geological and hydrogeological setting

The current geological state of knowledge of the Doñana aquifer can be attributed to the works of Salvany and Custodio (1995), Custodio and Palancar (1995) and Salvany and Custodio (2001). The first differentiated four different lithological units in the plio- quaternary materials of the central zone of the Lower Guadalquivir; these are the Deltaic Unit, Alluvial Unit, Marshes Unit and Aeolian Unit. The sand-dune ponds are located in the last-mentioned unit, which is characterized by being formed by aeolian, fluvial-aeolian and fluviomarine sands (Custodio and Palancar, 1995), shaping a very homogeneous layer along the entire coastal strip. Its thickness varies from about 150 meters on the coast to a few meters inland. The sands in this unit are variable: white, yellowish, orange with sizes between fine and medium. In the aeolian unit, intercalations of clayey silts and levels of peat coming from old ponds can coexist. This unit was extended from the northwest to the southeast, placing itself on the Deltaic Unit and the Marsh Unit.

The Doñana National Park is located at the Southeastern side of Hydrogeological Unit 05.51, also known as the Almonte-Marismas aquifer or Doñana Aquifer (Figure 3). The mentioned aquifer was named Aquifer 27 according to the old IGME nomenclature of 1970. It occupies 3,409 km² of the Guadalquivir River Basin (Suso and Llamas, 1993). It is limited to the North by the Rio Tinto and the Niebla-Posadas Aquifer, to the Northeast by the Guadiamar River, to the Southeast by the Guadalquivir River and the to the West by the Atlantic Ocean.

The aquifer has a confined area beneath the marshes, and an unconfined area formed by conglomerates in the area closest to the Tinto River and by sands where the sand-dune

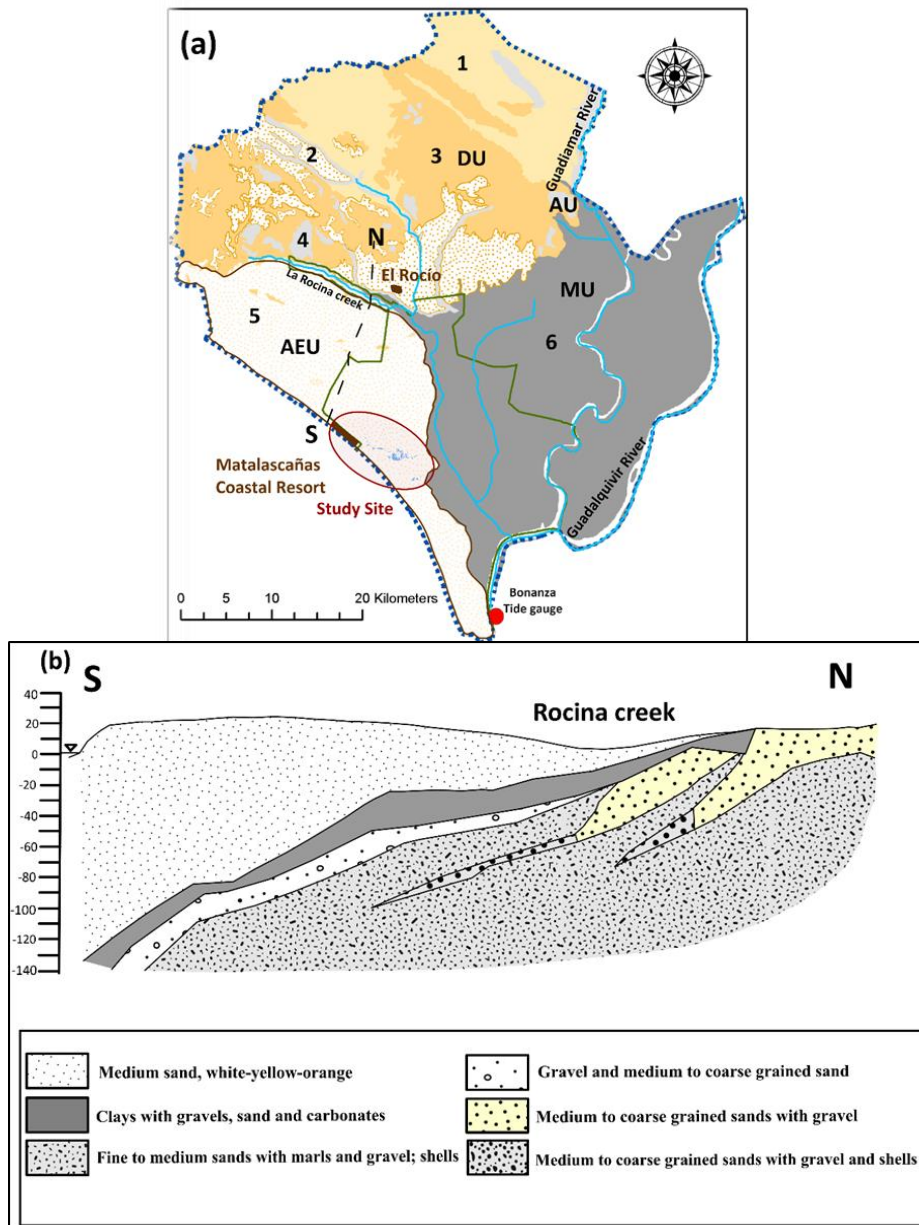


Figure 3: (a) Doñana aquifer and location of the study site. Lithology: 1. Calcarenites, Marls, Gypsum and Limestone (Upper Miocene-Pliocene); 2. Fossil dunes; 3. Sands and Marls (Pliocene); 4. Alluvial (Gravel, Sands, Marls and Clays). AU. Alluvial Unit; AEU. Aeolian Unit; DU. Deltaic Unit; MU. Marshes Unit. 5. Fine sands and coastal dunes; 6. Marshes. The boundaries of the National Park are delimited in green. The limits of the Dune aquifer in the Aeolian Unit are colored in brown. The geological cross section showed in figure b) is marked with a black line in figure a). (b) Lithological cross section (modified from Salvany et al. 2010).

ponds are located. Some authors refer to this sandy area of the unconfined aquifer as "Dune Aquifer" (Vela, 1984). Its surface, about 90 km², connects the Atlantic Ocean with the Guadalquivir marshes. A layer of Miocene marls forms the base of the aquifer (Salvany and Custodio, 1995). The values of the hydraulic parameters are variable in the Almonte-Marismas aquifer, as it is composed by multiple lithological units. In the area close to the marsh, the storage coefficients are close to 5×10^{-4} , while in the free subunit near the coast they are 3×10^{-2} . Transmissivity values range between 100 m²/day in the coastal fringe and 3,000 m²/day in the area closest to the ponds (IGME, 1992). The permeability values also vary greatly throughout the aquifer, fluctuating between 0.001 and 30 m/d (Guardiola-Albert et al. 2010).

The recharge is produced mostly by direct rainfall infiltration in the unconfined aquifer (in the western area). The average annual recharge rate in the Doñana Aquifer is 200 hm³/year (Guardiola-Albert et al. 2009) and in the Dune aquifer it takes place around the half of the total recharge. Recently, a lysimeter installed in a dune belt has estimated that the recharge amounted to 64% of the total precipitation registered (Kohfahl et al. 2019). The water outputs from the aquifer are either evapotranspiration, diffuse drainage to rivers or sea, pumping extractions for crop irrigation and urban water supply and finally, discharge to ponds. In these ponds, the largest water output is by direct evaporation (Lozano et al. 2002).

In administrative terms, the Guadalquivir River Basin Authority has divided the Almonte-Marismas Aquifer into 5 subunits: "Almonte", "Marismas", "Marismas de Doñana", "Manto Eólico de Doñana", and "La Rocina" (BOE, Real Decreto 1, 2016). "La Rocina", "Almonte" and "Marismas" are at risk of not achieving a good quantitative status according to the latest announcement of the Guadalquivir River Basin Authority (BOE Anuncio 39064, 2019). Furthermore, "La Rocina" is also at risk of not achieving a good qualitative status, according to the same

announcement. The ponds studied are located in the "Manto Eólico Litoral de Doñana", which has water table values below than the expected, but not sufficiently depressed to be considered as an aquifer at risk, as stated in the latest available report of the Guadalquivir River Basin Authority (2019). The whole Doñana Aquifer is in a "Pre-Alert" status according to the aforementioned report.

The main surface watercourse providing water resources to the Doñana National Park is La Rocina stream. It is fed by the aquifer discharge and provides water to the marsh. However, in the study area where the ponds are located, there are no surface watercourses.

1.4.4. Characteristics of the studied ponds

Most of the sand dune ponds in Doñana are temporary, or in other words, water bodies with a recurrent desiccation phase (Williams, 2006). This is the case of the Zahíllo, Taraje and Sopotón ponds (Figure 4), three of the four studied ponds. Santa Olalla pond, the fourth of the studied ponds, is the only natural water body in the Doñana Natural Area with a permanent hydroperiod. There are other permanent water bodies, named "zacallones", which are anthropic small excavations in the terrain of 2-4 meters of maximum depth that reach the water table. Traditionally, they have been used by cattle to drink water throughout the whole year.

The characteristics that best define the temporary ponds are their variability and unpredictability (Díaz-Paniagua *et al.* 2015) since the duration of their flood cycles is directly dependent on the annual rainfalls. The type of species and abundance of organisms that inhabit the ponds depend on hydroperiod of each of the ponds. The ponds are formed in ground depressions, in preferential zones of groundwater discharge. Generally speaking, temporary ponds are no deeper than 1.5 meters. In case these levels are exceeded, the water overflows to nearby areas of lower altitude. Santa Olalla pond has a maximum depth of just 3 meters. When this

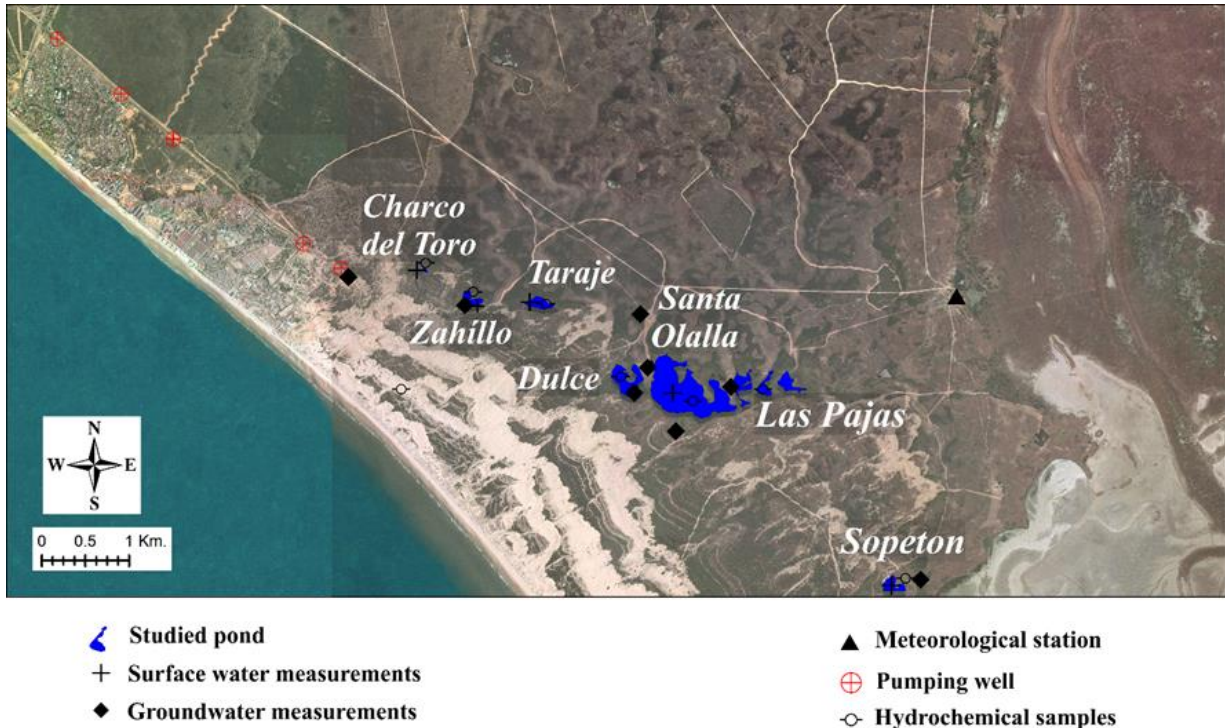


Figure 4: Study site. All of the ponds studied here are colored in blue. The pumping wells located at the coastal resort are also marked.

height is reached, it joins with the adjacent ponds Dulce and Las Pajas, shaping a single water body. This situation only takes place in very rainy years such as in 2012. The natural origin of the ponds and their great abundance and heterogeneity make them a unique ecosystem of great scientific and recreational interest in Europe (Scheffer *et al.* 2015).

These conditions also provide suitable habitat characteristics for some groups of species, such as amphibians, for which the ponds are an optimal place of reproduction (Gomez-Rodríguez *et al.* 2012), and for aquatic macroinvertebrates, mainly odonates, since their life cycle is closely linked to the temporality of the ponds. Thus, the presence of such group of species are indicator of a good state of the ponds (Briers and Biggs, 2003). Of the eleven amphibian species that exist in Doñana (three urodeles and eight anurans), five are Near Threatened (NT) according to the IUCN (International Union for Conservation of Nature).

On the other hand, due to the fact that Doñana has large number of hours of solar radiation, the ponds show high fertility. In spring, phytoplankton has significant

development, in which contaminants do not play any role, given that there are not fertilizers pollution in in the study site.

The ponds are also habitat to many vertebrates which require water bodies for their existence: amphibians such as perez's frog or southern marbled newt; reptiles such as freshwater turtles and water snakes; mammals such as the water rat and the otter; aquatic birds such as real ducks, herons and egrets. The fish are not characteristic of temporary environments, although they can reach them after periods of significant floods in which the ponds and the marsh (with fishes) are connected. The advantage of temporary over permanent habitats is that in the former there are fewer predators (such as fishes) that can potentially threaten the larvae of amphibians and dragonflies.

The vegetal species situated in the ponds border can also be used as indicators of hydrological changes (Sousa *et al.* 2009; Muñoz-Reinoso (1995, 1996, 2001a, 2001b). The vegetation belt is usually composed of helophytic species (they are in need of flooded soil to grow) and hydrophytes (they require phreatic water). In a study carried out

in the Dulce (of long hydro-period), Zahíllo, and Charco del Toro ponds, it was found that only the Dulce pond had not changed the distribution of its vegetation belt. In the outer zone of the helophytic and hydrophytic vegetation, there was a ring of terrestrial vegetation typical of the white forest. The

only change was the progressive absence of the helophyte *Scirpus lacustris*. The basin of the Zahíllo pond is currently covered with 50% hydrophilic vegetation and in the case of the Charco del Toro pond, the terrestrial vegetation that has colonized its basin

1.5. Methodology

1.5.1. Hydrodynamic methods

Water balance is a commonly used method to understand the conceptual model of an aquatic system that has been used in multiple studies about wetlands. The water balance technique applies the law of conservation of mass (Rose, 2004). According to this principle, differences between water inputs and outputs are accounted for changes in storage. Thus, the simplified water balance equation is:

$$\text{Water inputs} = \text{Water outputs} \pm \text{Change in Storage (1)}$$

Moral *et al.* (2013) and Rodríguez-Rodríguez and Schilling (2014) applied this methodology in Los Jarales playa-lake and Ballestera and Calderon playa lakes, respectively (Andalusian lowland countryside), located in the Guadalquivir River Basin. The calibration of the soil water budget and the water inputs into the pond was made by means of climatic data, water storage measurements, the topographic divide and the lake morphometry in the mentioned playa-lake. These authors were able to estimate, at a monthly and daily time step, the percentage of surface runoff and groundwater flow, considered as water inputs.

In this study, the conceptual model developed by Rodríguez-Rodríguez *et al.* (2016) for shallow ponds was adapted in order to define the components of the water budget in the Zahillo, Santa Olalla and Sopotón ponds following the equation based on the general water balance equation:

$$\text{GWNF} = E - P \pm \Delta S \quad (2)$$

where Groundwater net flux (GWNF) is the incognita in the water balance equation; E is the direct evaporation from the water surface; P is direct rainfall in the ponds; and ΔS is the change in the water stored. Taking into account the high permeability of the

sands, surface runoff does not need to be accounted for in the water balance equation.

Evaporation (E) was estimated following Penman formula (Penman, 1956), which is a semi-empirical equation combining mass transfer and energy budget methods. According to McMahon *et al.* (2013), this is the most accurate method to calculate outputs by evaporation from shallow water bodies. Data needed to calculate E are the daily values of air temperature, the relative humidity, the solar radiation and the wind speed, as well as other parameters calculated from these variables.

Daily precipitation (P) data used for the water balances were collected from the meteorological station “AlmonteDonana” from the Spanish Meteorological Agency (AEMET), located inside the Doñana Biological Reserve, just 3 km from Santa Olalla pond.

The changes in the water storage (ΔS) were recorded by sensors. To carry out volumetric water balances, hypsometric curves were calculated. Sensors which measure the total pressure at a 3-h time step were used to conduct the water-level monitoring. These sensors, of different typologies, were installed in each of the piezometers and ponds (Figure 4). Barometers were installed nearby to compensate the measurements of the mentioned sensors (See chapter II for further details).

The hypsometric curve of a pond relates the horizontal cross sectional area of the pond basin to the water level recorded by sensors. The curves were calculated using the equation developed by Hayashi and Van der Kamp (2000). It was used to estimate the surface of each of the ponds at a daily time step and as a consequence, the volumetric variation in each of the pond.

The water balance calculations for the three ponds were carried out in three time periods: firstly, for the years 2015 and 2016, secondly between December 2016 to June 2017 and lastly from February to June 2018. The last two periods were adapted to the flooding period of the Zahillo pond for comparison purposes.

Moreover, hydraulic gradients were estimated using the water table data from four piezometers close to the pond and the pond itself, following the Equation 2:

$$HG=(\Delta h/\Delta x) \quad (3)$$

where Δh is the difference between the daily water table in each piezometer and the water level in the Santa Olalla pond (in m asl) and Δx is the distance from each piezometer to the pond. Data used were as well at a three hourly time step and were measured by Diver and Level-logger sensors.

The semi-diurnal tidal oscillation observed in two medium-depth piezometers (see Fernández-Ayuso and Rodríguez-Rodríguez, 2018 for further details) allowed the estimation of transmissivity and permeability by tidal delay and tidal efficiency factor methods. Diver sensors installed into them were programmed to measure the oscillations of the water table during two weeks (28/11/2017- 13/12/2017). The measurements taken by the sensors were compensated by barometers to obtain final water tables values. Sea level data used were obtained by the tide gauge “Bonanza 2”, located at the Guadalquivir River mouth, 24 km from the study site.

A time period of three days has been used to apply the methods of tidal delay and tidal efficiency factor, in December, the 7th to 9th, 2017. The estimation of transmissivity and permeability as a function of the tidal data has been carried out by applying the equations of the response model to the tides developed by Sánchez-Úbeda *et al.* (2012) and applied by

Sánchez Úbeda *et al.* (2013) and Nieto-López *et al.* (2016). These equations are:

A) Delay of the oscillation of the piezometric level with respect to the oscillation of the tides:

$$R = \frac{x}{2} \sqrt{\frac{t_0 S}{\pi T}} \quad (4)$$

where R is the delay or lag (hours) that take place between the tide signal and its effect in the water table, x is the distance from the point to the coastline (in meters), and t_0 is the period of oscillation of the tide (12.5 hours). The transmissivity value is obtained through different storage coefficient values (S) assigned.

B) Tidal Efficiency:

$$EM = \exp\left(-\sqrt{\frac{\pi x^2 S}{t_0 T}}\right) \quad (5)$$

The EM value is the quotient between the amplitude of the oscillation of the water table and the tidal amplitude. The amplitude values of the oscillation of the water table and the tides have been obtained by means of the method of average amplitude (Jha *et al.* 2003) as well as by the calculation of the average values of amplitude between the correlated maximums and minimums in the study period. From the transmissivity values, permeability has been calculated ($K = T / b$, “b” being the saturated thickness).

I.5.2. Thermal and hydrochemical methods

Thermal methods as an approach to establish relationships between surface water and groundwater began to be developed at the beginning of the 20th century. However, the results obtained in practice presented problems concerning the technological limitations in the data collection and analysis (Rosenberry and LaBaugh, 2008). The

computational progress and the development of adequate software to model the results obtained led to a rise in the use of this methodology, which is both reliable and inexpensive. As laboratory treatment is not required before the data analysis, it is considered as a faster tool than chemical tracers (Stoneman and Constantz, 2003). Thus, heat as a tracer to establish surface water-groundwater interactions has been increasingly used as a tool in recent years (McCallum *et al.* 2012; Rau *et al.* 2014).

Several authors used thermal methods in their research carried out in the Doñana area, acknowledging the advantages of this technique. Some examples are the studies of Custodio (2011), and Ramos-Fuertes (2012). Custodio applied a 1-D vertical model using temperature loggers installed in deep piezometers and detected that changes in the land use from natural vegetation to grazing or crops often caused soil warming. During recharge episodes, the increased soil temperature can be found in deeper layers of the soil. On the other hand, Ramos-Fuertes accomplished a thermal balance in the Doñana marshes in which it was revealed the high water sensitivity to changes in the heat transmitted. Furthermore, during spring and summer, the importance of evaporation processes in the balance increased.

The application on thermal methods in this thesis had three stages. In the first place, there were three field campaigns of E.C. and temperature during three different time periods: July 2016, May 2017 and May 2018, after a rainy period. In this last mentioned campaign, the measurements were taken on the northwestern shore of the pond and in it, pH values were taken as well. For more details, see Chapter III and Rodríguez-Rodríguez *et al.* (2018).

With regard to the second stage of the study, a wire with four auto logging temperature sensor, called iButtons, fixed at different depths, was installed inside a PVC tube. The iButtons were programmed to

record temperature data at an hourly time step. Finally, the software 1D-Temp-Pro V.2. (Koch *et al.* 2015) was used for the analysis of one-dimensional vertical temperature profiles. It has been modelled one period during high water levels (from February to May 2017 and one during low water levels (October 2017 to March 2018). The program allows users to calibrate VS2DH models against measured data to estimate vertical groundwater/surface-water exchange. The modelling conditions were as follows: porosity was set as $0.3 \text{ m}^3/\text{m}^3$ (Fernández-Ayuso and Rodríguez-Rodríguez, 2018), thermal conductivity $1 \text{ W/m}^\circ \text{C}$, sediment heat capacity $3.3 \times 10^6 \text{ J/m}^3$ (Goto and Matsubayashi, 2008) and dispersivity $5 \times 10^{-4} \text{ m}$ (Jensen *et al.* 1993)

Furthermore, hydrochemical characterization is often used by hydrologists as a supplementary tool to understand the wetlands hydrodynamics. Sacks (1989), Sacks *et al.* (1992), Manzano *et al.* (2008; 2013) and Kohfahl *et al.* (2014; 2015) are some of the authors who studied the hydrochemistry in the Doñana aquifer and the dependent wetlands. Sacks applied a hydrochemical model in Dulce-Santa Olalla-Pajas system using major ions and isotopes analysis and estimated the saturation indices in both, surface water and the groundwater nearby these water bodies. Manzano, characterized the hydrochemistry in various sectors of the Almonte-Marismas aquifer. Finally, Kohfahl took oxygen measurements with a fibre-optic probe in shallow groundwater nearby ponds of Doñana National Park. Moreover, he detected arsenic in surface water in the east of the study site.

For the hydrochemical characterization in this thesis, carried out during different field campaigns, physico-chemical parameters (water temperature, pH and C. E.) of the water were measured in situ, with a portable multi-meter (HANNA®). Surface water samples were taken both, in the shore and in the center of the pond and the groundwater samples at a depth of approximately one meter below the water table. Afterwards, they were conserved in plastic bottles of 0.5 l. transferred in cold to

the Hydrochemistry Laboratory of the Pablo de Olavide University, where they were analyzed in the following days. Analysis of major components of the more than 150 water samples taken in 7 studied ponds (Zahillo, Sopetón, Taraje, Zacallón Charco del Toro, Santa Olalla and Dulce) and in 7 piezometers nearby, has been carried out by ion chromatography (ICS-1000, DIONEX®). The bicarbonate analysis was done by colorimetric evaluation.

The isotopic water analysis was carried out in the laboratories of the Hydrogeology

Center of the University of Malaga. The analysis of the results obtained was accomplished using AquaChem © (Waterloo Hydrogeologic) software for the establishment of the hydrochemical database and the R package “vegan” (Oksanen *et al.* 2018) for the statistical analysis of the results. The saturation indexes have been calculated with PHREEQ-C software version 3 (Parkhurst and Appelo, 2013).

I.5.3. Time series analysis

Time series analysis has gained in importance in hydrological science over time. It comprises a very broad spectrum of techniques. In this thesis, two of them have been used: Prophet and wavelet analysis.

The Prophet model (Taylor and Lehman, 2018a) has a very recent use in the field of hydrology. One of its main advantages is its capacity of distinguishing between the periodic and the non-periodic components of the time series. Papacharalampous *et al.* (2018) applied this model for the first time to hydro-meteorological series. They compared the forecast obtained with the Prophet model with the modelled results obtained from the conventional techniques such as ARFIMA or Theta. They concluded that Prophet is a competitive model, especially if it is complemented with more established methods. More recently, Aguilera *et al.* (2019), applied the Prophet model to the time series recorded in deep piezometers located in Doñana National Park, very close to Matalascañas Coastal Resort.

The wavelet analysis has been used since 1990 (Sang, 2013). It was developed by Grossman and Morlet (1984). One of the main advantages of wavelet analysis is the possibility of performing a multi-temporal analysis, in which periods with significance can be distinguished in a given time (Sleziak *et al.* 2015). In this way, complex processes derived from a wide range of effects, e.g. rainfall, tides or groundwater pumping, can be distinguished. Wavelet analysis had never been applied before in the Doñana area, despite having a wide use in diverse hydrogeological contexts (Moutahir *et al.* 2017; Kang *et al.* 2007; Labat *et al.* 2004).

In this thesis, the time period selected to carry out the time series analysis was 06/24/2016-01/15/2018. The dataset used contained rainfall data, groundwater levels from piezometers different depths (shallow, medium and deep) as well as from a pumping

well located at the Matalascañas coastal resort. Santa Olalla pond surface water level and sea level were also measured from a nearby tide gauge station. For more information, see Chapter IV and the article of Fernández-Ayuso *et al.* (2019).

The visual and descriptive analysis of the time series was the first step followed. Secondly, a time series decomposition into relevant periodic seasonal components was carried out with the Prophet model (Taylor and Lethman, 2018a). Finally, continuous wavelet analysis of high-frequency components in the time-frequency domain was implemented.

Prophet is based on an additive model applied on a time series ($y(t)$) where linear growth trends ($g(t)$) are fitted with periodic seasonalities ($s(t)$), plus a normal random error term ($\epsilon(t)$):

$$y(t) = g(t) + s(t) + \epsilon(t) \quad (6)$$

We used this model in the R Package Prophet (Taylor and Letham 2018b). The trend was resolved as follows: S changepoints (dates where the growth rate is allowed to change) are modeled using a vector of rate adjustment. Prophet specifies a sparse prior $\delta_j \sim \text{Laplace}(0, \tau)$ on the magnitudes of the rate changes. The parameter τ controls the flexibility of the model to choose potential changepoints at which the rate is likely to change. Large values will make the trend more flexible and will allow many changepoints. Seasonal components are fitted using a partial Fourier sum on the corresponding periodicity (365.25 days for yearly component, 7 days for weekly component, etc.) with coefficients estimated from a normal smoothing prior distribution $\beta \sim N(0, \sigma^2)$. The default values for the parameters set by the developers were also found to be suitable for our data: $\tau = 0.05$, $\sigma^2 = 10$, 10 Fourier terms for the yearly periodic component, three Fourier terms for weekly periodic component and four Fourier terms for daily periodic component.

On the other hand, time-frequency analysis was performed through continuous wavelet analysis using the R package WaveletComp (Roesch and Schmidbauer, 2018). WaveletComp analyzes the frequency structure of univariate and bivariate time series using the complex-valued Morlet wavelet transform:

$$\phi(t) = \pi^{-1/4} e^{i\omega t} e^{-t^2/2} \quad (7)$$

It allows a continuous, complex-valued wavelet transform of the time series, and is

therefore an information-preserving tool that can be applied to select any time and frequency resolution parameter. In order to analyze non-stationary periodic components of the series in the time-frequency domain, and complement the previous analysis of seasonal components, continuous wavelet analysis was performed on the differenced data (i.e. $x_t - x_{t-1}$, $t = 2, \dots, n$), where n is the length of the series. This allows comparison of water level lags among monitoring points, and the ability to focus on the higher-frequency components of the series.

Chapter II: Hydrodynamic methods



II.1: Groundwater input quantification to Santa Olalla pond by means of daily water balances (Doñana National Park, Huelva)

Cuantificación de los aportes hídricos subterráneos a la laguna de Santa Olalla a partir de balances hídricos diarios (Parque Nacional de Doñana, Huelva).

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ABSTRACT

In this project, a daily water balance in Santa Olalla interdunal pond, one of the few ones with permanent hydroperiod in Doñana National Park, has been made. The balance was made by determining the water inputs and outputs, using meteorological data from nearby stations as well as three-hourly interval data of the water level in the pond. The results indicate a groundwater input of 0.39 hm³ to the pond from January 2015 to March 2016, compared to 0.11 hm³ by direct precipitation. The groundwater level in nearby piezometers located on the dune aquifer remained above the water level of the pond during the study period. Maintaining the water table levels in the unconfined aquifer is of vital importance to assure the groundwater input to the pond in the future. For this reason, groundwater withdrawals in this unique ecosystem must be monitored and appropriately managed. Key-words: Wetlands, surface water – groundwater interaction, Doñana N.P.

Key-words: Wetlands, surface water – groundwater interaction, Doñana N.P

RESUMEN

En este estudio se ha realizado un balance hídrico a escala diaria en la laguna de Santa Olalla, una de las pocas lagunas de hidropériodo permanente del Parque Nacional de Doñana. El balance volumétrico se ha realizado determinando las salidas y entradas a partir de los datos meteorológicos de estaciones cercanas y de los registros trihorarios del nivel del agua de la laguna. Los resultados indican unos aportes por escorrentía, mayoritariamente subterránea, a la laguna de 0,39 hm³ desde enero de 2015 a marzo de 2016, frente a 0,11 hm³ de entradas por precipitación directa. El nivel freático en piezómetros cercanos, ubicados en las arenas del manto eólico, se mantuvieron por encima de la cota de lámina de agua libre de la laguna durante el periodo de estudio. El mantenimiento de estos niveles en el acuífero libre es de vital importancia para que no se comprometa esta aportación subterránea en el futuro, para lo cual se debe controlar y mantener la vigilancia de las extracciones de agua subterránea en el entorno de este ecosistema singular.

Palabras clave: Humedales, relación aguas superficiales – aguas subterráneas, P.N. Doñana.

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II.1.1. Introducción

Las extracciones de aguas subterráneas en el área de Doñana han provocado un impacto hidrológico en algunas zonas del Parque, tal y como advierten desde hace varios años diversos organismos (Custodio *et al.* 2009). El acuífero de Doñana se extiende por unos 2600 km² de las provincias de Huelva y Sevilla. Este territorio depende en gran medida de las aguas subterráneas para el abastecimiento a poblaciones y para el regadío de cultivos. Sobre este acuífero se sitúa el Espacio Natural de Doñana, que posee una superficie protegida (Parque Nacional y Parque Natural) próxima a 1080 km². Muchos de los ecosistemas de Doñana

los descensos piezométricos originados por la extracción de aguas subterráneas están produciendo cambios en la vegetación, la desecación o disminución de los niveles de agua en lagunas próximas a Matalascañas, así como la disminución de los aportes hídricos a arroyos. (i.e. Serrano y Serrano, 1996; Muñoz Reinoso, 2001; Serrano *et al.* 2008; Custodio *et al.* 2009; Manzano *et al.* 2009). La laguna de Santa Olalla se sitúa en la zona de reserva biológica del Parque Nacional, a sólo 4 km de la población de Matalascañas. Es la más extensa de las numerosas lagunas existentes en relación con el manto eólico de Doñana. Como se puede observar en la figura 1, forma parte del sistema lacustre Dulce-Olalla-Las Pajas, ya

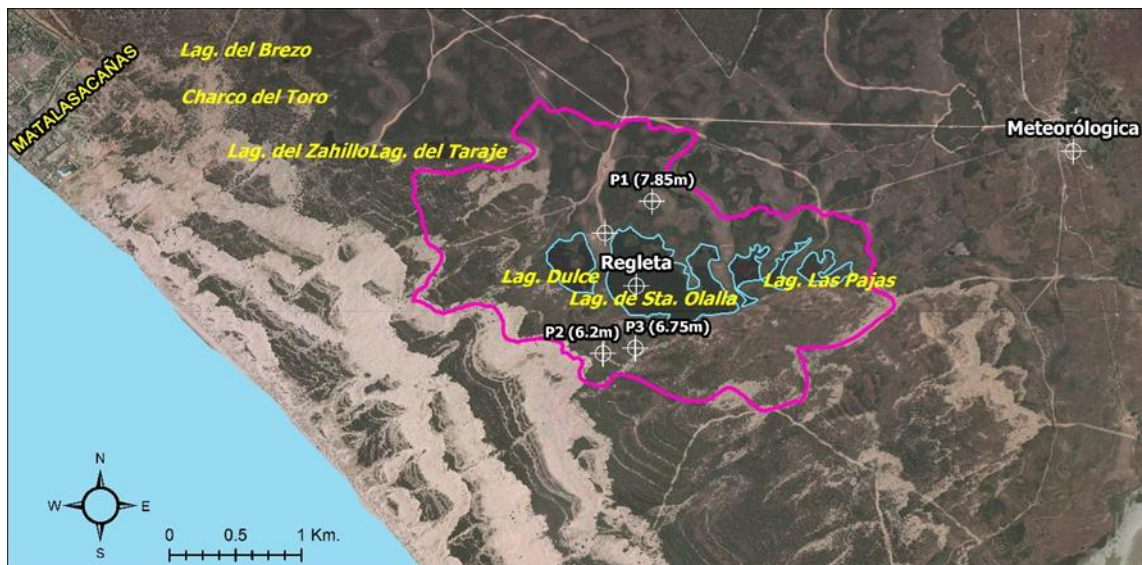


Fig. 1.- Localización de las lagunas de Santa Olalla, Dulce y de Las Pajas, de los piezómetros P1, P2 y P3, y la estación meteorológica del Palacio de Doñana. Asimismo, se señala la ubicación de otras lagunas asociadas al manto eólico de Doñana (Brezo, Charco del Toro, Zahíllo y Taraje) y del núcleo urbano de Matalascañas. En violeta, la delimitación de la cuenca superficial del sistema Dulce-Olalla-Las Pajas.

Fig. 1.- Location of Santa Olalla, Dulce and Las Pajas ponds and P1, P2, P3 piezometers and Palacio de Doñana weather station. Also the location of other ponds associated with the sand dunes of Doñana (Brezo, Charco del Toro, Zahíllo and Taraje) and the town of Matalascañas. The delimitation of the surface basin of the system Olalla-Dulce-Pajas is shown in purple.

dependen de las aguas subterráneas, que en amplios sectores se encuentran a muy poca profundidad. Los acuíferos también alimentan a numerosas lagunas estacionales y permanentes y a los principales arroyos de la zona Olías Álvarez y Rodríguez-Rodríguez, 2013. Existen evidencias de que

que en épocas de aguas altas todas estas lagunas forman un cuerpo de agua continuo. La cuenca superficial del sistema Dulce-Olalla-Pajas tiene una superficie total de 500 ha (Fig. 1).

En las inmediaciones de la laguna se han perforado tres piezómetros someros (P1, P2 y P3). También se muestra la localización de un sensor de C.E., temperatura y presión de la columna de agua, instalado en la zona más profunda de la laguna y la situación de la estación meteorológica del Palacio de Doñana. Cabe mencionar, por último, la proximidad de la línea de costa (2,6 km) a la laguna. El objetivo de este trabajo es la realización de un balance hídrico a escala diaria de la laguna de Santa Olalla, una de las pocas de hidropereodo permanente de Doñana, para determinar en qué medida esta laguna es dependiente de las aportaciones

subterráneas del acuífero del manto eólico. El balance volumétrico, realizado a partir de datos meteorológicos y de los registros del nivel del agua medidos en la regleta de la laguna, ha permitido una notable mejora del conocimiento de su funcionamiento hídrico, así como la cuantificación de las principales entradas y salidas de agua al sistema hídrico. Finalmente, las medidas de temperatura y conductividad eléctrica del agua y el análisis químico de las muestras tomadas en los piezómetros y en la laguna han permitido la caracterización físico-química de las aguas subterráneas y superficiales de la zona de estudio.

II.1.2. Materiales y métodos

En cada uno de los piezómetros comentados anteriormente se han colocado sensores de nivel de agua (Diver®), programados para tomar medidas trihorarias de niveles de agua subterránea. Por otro lado, en la regleta de la laguna se ha instalado un sensor de tipo CTD, capaz de medir la conductividad eléctrica, temperatura y profundidad de la lámina de agua, programado para hacerlo también de forma trihoraria. El análisis químico de componentes mayoritarios en las muestras de agua tomadas en la laguna de Santa Olalla se ha realizado mediante un cromatógrafo iónico DIONEX, modelo ICS1000. Se ha empleado el programa TRASERO (Padilla y Delgado, 2012), para la estimación de la escorrentía para diferentes capacidades de campo. Las entradas por precipitación (P) se han calculado a partir de los datos de estaciones meteorológicas cercanas (Almonte-Rocío y Palacio de Doñana), una vez analizadas y corregidas las series. Para calcular las salidas por evaporación (E) se ha aplicado la fórmula original de Penman (1956), que según McMahon *et al.* (2013) es el método más adecuado para lagunas someras, y que ha dado buenos resultados en otras lagunas de la cuenca baja del río Guadalquivir (Rodríguez-Rodríguez *et al.* 2016). Los cambios de volumen de agua almacenado en la laguna ($\Delta\theta$) se han determinado a partir de los registros de nivel medidos en la regleta de la laguna. La escorrentía (Esc.) se ha calculado por diferencia, mediante la ecuación: $Esc. = E - P \pm \Delta\theta$. Todos los componentes se han determinado en mm/día. Para el cálculo de dichos componentes en volumen se ha utilizado la curva hipsométrica de la cubeta lacustre.

II.1.3. Resultados

Durante el periodo de estudio, las entradas de agua a la laguna se han producido por precipitación directa sobre el vaso lacustre y por escorrentía que, dada la elevada permeabilidad de los materiales arenosos sobre los que se ubica la laguna, es mayoritariamente subterránea. Las salidas se han producido casi exclusivamente por evaporación desde la lámina de agua superficial. En la figura 2 se observa la variación de niveles en cada uno de los piezómetros, así como la variación del nivel de la laguna durante el periodo de estudio. La cota piezométrica en el acuífero se sitúa entre 2 y 4 m por encima de la cota de la laguna. Se aprecia que el piezómetro 1, situado al N, registra subidas de nivel al comienzo del periodo de estudio menos pronunciadas que los otros dos piezómetros, situados al S. Por otro lado, cabe resaltar que tanto el nivel de la laguna como el de los piezómetros experimenta una subida en los valores registrados en los meses de enero a mayo, que coincide con un periodo de abundantes precipitaciones (Fig. 3). A partir de esa fecha, los piezómetros, de 1 m de profundidad, no registran nivel. En la figura 3, se muestra la evolución de las precipitaciones, conductividad eléctrica, nivel de la laguna y temperatura del agua. A principios del periodo de estudio, invierno de 2015, se registran fuertes precipitaciones que llegan a superar 4 cm diarios, lo que se traduce en una importante subida del nivel del agua de la laguna en torno a 50 cm. Por ejemplo, el 18 de enero de 2015 desde las 9h hasta las 12h se produce un aumento del nivel del agua de 9 cm y un ascenso paulatino hasta mayo de 2015. Desde mayo de 2015 a octubre del mismo año, se produce un descenso del nivel (0,8 m en total). Las precipitaciones ocurridas en el otoño de 2015 provocan un aumento del nivel de casi 30 cm.

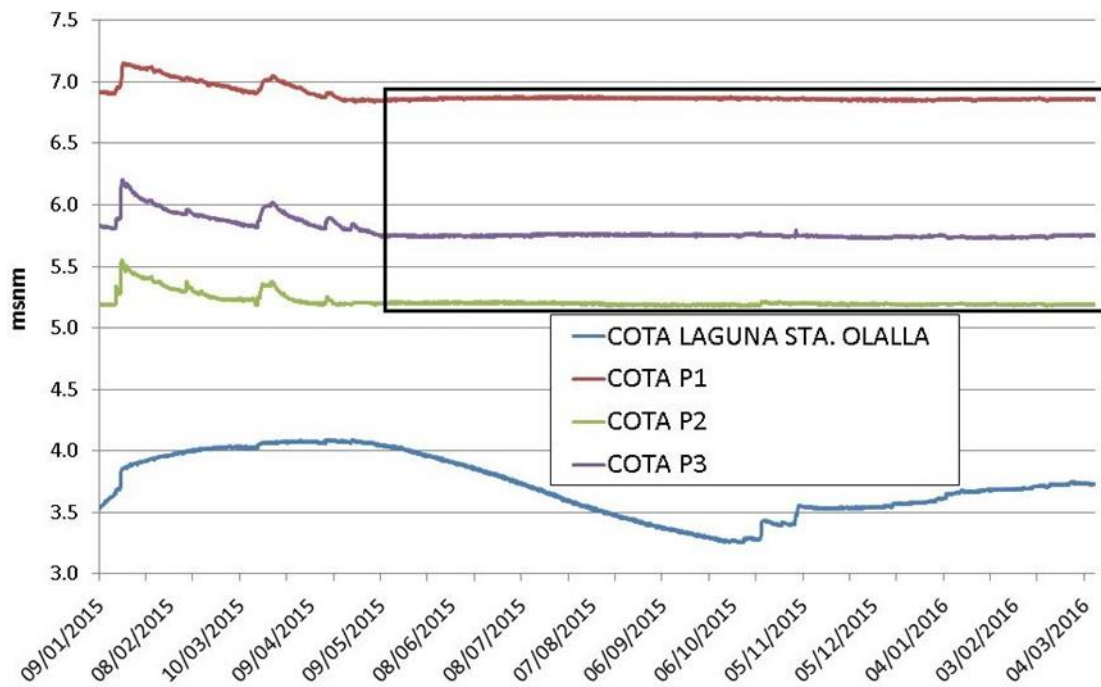


Fig. 2.- Evolución de los niveles de agua en los piezómetros (P1, P2 y P3) y en la laguna de Santa Olalla. *A partir de mayo de 2015, y hasta el final del periodo de estudio, los piezómetros someros (1 m de profundidad) no registraron nivel (ver recuadro). En cualquier caso, se comprobó que los niveles no descendieron bajo la cota de la laguna en piezómetros cercanos instalados por el IGME.

Fig. 2.- Evolution of the water level in the piezometers (P1, P2 and P3) and in Santa Olalla pond. *From May 2015 until the end of the study period, shallow piezometers (1 m deep) did not show any level record (see box). Anyhow, levels did not fall below the pond level in nearby piezometers installed by the IGME.

A partir de este momento y hasta principios de marzo hay un ascenso suave del nivel de 20 cm. En el caso de la temperatura, se observa una oscilación anual, con valores máximos en verano (29,8°C) y mínimos en invierno (9,44°C), así como una bajada de temperaturas cuando se producen precipitaciones. Los valores de conductividad eléctrica del agua experimentan una importante subida de más de 5 mS/cm a finales de enero de 2015 hasta principios de febrero de 2015, momento en el cual empiezan a disminuir de forma progresiva hasta julio del mismo año. A partir de ahí la conductividad se mantiene estable en torno a los 5 mS/cm, hasta el final del periodo de estudio. Los resultados del balance hídrico, expresados como valores acumulados del volumen (m³) se pueden observar en la figura 4, distinguiéndose las

entradas (precipitaciones y escorrentía) de las salidas (evaporación) y la variación acumulada en el almacenamiento a escala diaria. La escorrentía se ha calculado a partir de la fórmula del balance hídrico ($Esc. = E - P \pm \Delta\theta$). Se observa un incremento progresivo de la escorrentía, por lo que la entrada de agua a la laguna por esta vía es constante. Existen tres momentos en los que se observan incrementos mayores en el nivel, que corresponderían con episodios de entrada por escorrentía superficial. Las salidas en este caso son debidas a la evaporación y, en ocasiones, a la descarga de la laguna al acuífero, como se puede observar en los descensos en la escorrentía de finales de octubre a principios de noviembre de 2015. Las entradas por precipitación directa fueron de 399 mm (equivalentes a 0,118 hm³).

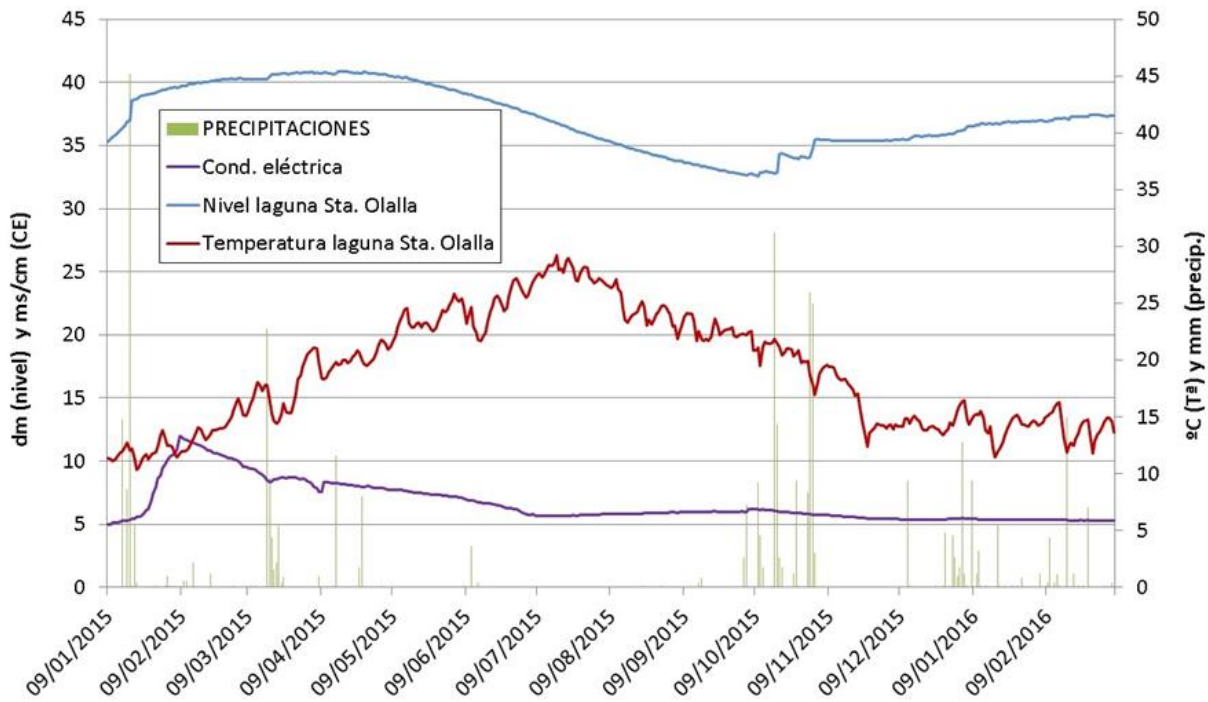


Fig. 3.- Serie de precipitaciones en el periodo de estudio registradas en la estación meteorológica del Palacio de Doñana. Evolución de la conductividad eléctrica, nivel (dm sobre el nivel del mar) y temperatura del agua en la laguna de Santa Olalla.

Fig. 3.-Series of rainfall during the study period recorded in the weather station Palacio de Doñana. Evolution of the electrical conductivity, stage (dm above sea level) and temperature of the water in Santa Olalla pond.

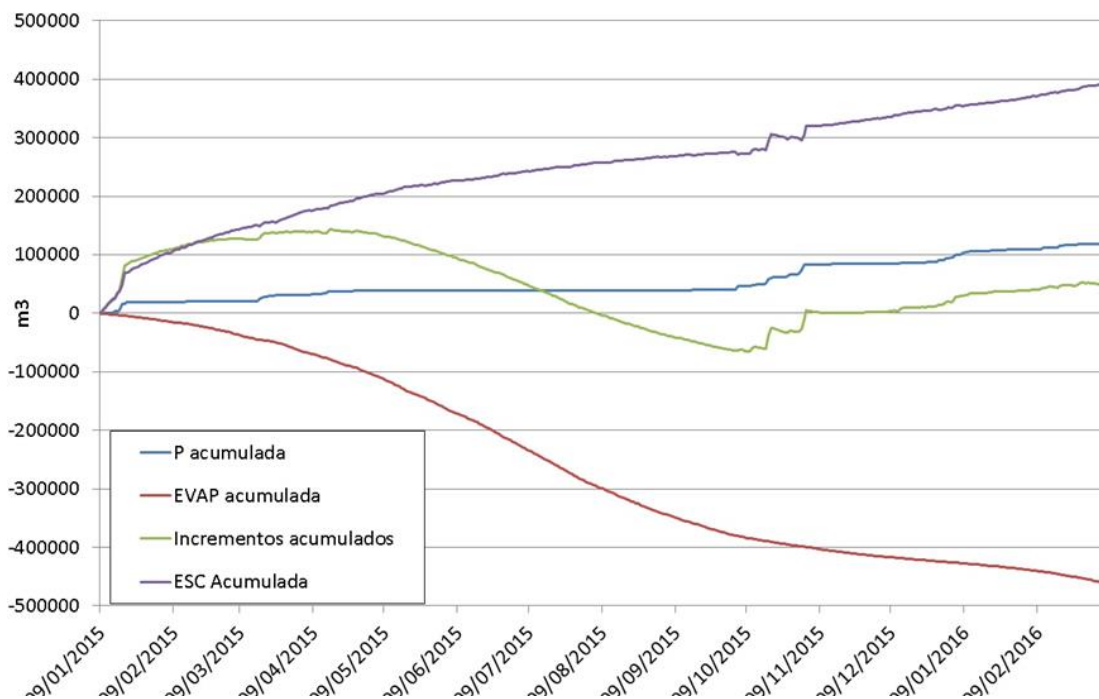


Fig. 4.- Balance hídrico diario. Los valores se presentan como acumulados de las precipitaciones, evaporación, almacenamiento y escorrentía.

Fig. 4.- Daily water balance. Data set is presented as accumulated values of rainfall, evaporation, storage and net groundwater flux.

Los volúmenes de escorrentía calculados mediante el balance fueron de 0,392 hm³, mientras que la salida mayoritaria se produjo por evaporación, 1810 mm (equivalentes a 0,461 hm³). El incremento en almacenamiento ($\Delta\theta$) fue moderado. La conductividad eléctrica media del agua de la laguna fue de 6,65 mS/cm y la mediana de 5,92 mS/cm. La temperatura fue relativamente elevada (18,67°C de media), estando por encima de la temperatura del aire (16,84°C) la mayor parte del año. La profundidad media de la laguna fue de 1,27 m. La máxima profundidad alcanzada fue de 1,64 m (abril de 2015) y la mínima 0,8 m (noviembre de 2015). Las aguas de la laguna son de tipo clorurado sódicas, con una salinidad total de 4086 mg/l. Por otro lado, las aguas subterráneas próximas a la laguna, muestreadas en los piezómetros, son dulces, de tipo bicarbonatado-sódicas con una salinidad media de 183,14 mg/l.

II.1.4. Discusión

Si bien el acuífero de los mantos eólicos está formado fundamentalmente por arenas (dunas), también hay depósitos menos permeables a diferentes profundidades (limos orgánicos y arcillas), lo que influye en que este sistema sea hidrogeológicamente complejo (Custodio *et al.* 2009). La formación de lagunas temporales en determinadas zonas está condicionada, por tanto, por ser sectores de descarga local de las aguas subterráneas del acuífero y, probablemente, por la presencia de materiales de baja permeabilidad en profundidad. Tal y como ya se comprobó a comienzos de la década del año 2000 mediante métodos isotópicos e hidroquímicos (Lozano, 2004; Lozano *et al.* 2001; Lozano *et al.* 2002) la laguna de Santa Olalla recibe una importante contribución de las aguas subterráneas del acuífero libre de los mantos eólicos. En este trabajo, se ha constatado que esta alimentación alcanza el 78% del total de las entradas durante el periodo de estudio, asumiendo que la totalidad de la escorrentía necesaria es de origen subterráneo. Tan solo en momentos

puntuales de elevada descarga y entradas por precipitación a la laguna, se aprecia que la laguna recarga el acuífero. Estos periodos de infiltración se traducen en un cambio de la pendiente en la curva de escorrentía acumulada (e.g. tras las fuertes precipitaciones de octubre de 2015). Aun así, es la evaporación directa la responsable de las principales salidas hídricas del sistema (>95%). Esta es la razón por la cual las aguas de la laguna son salobres: la entrada se produce con aguas subterráneas y de lluvia de baja salinidad (< 0,2 g/l) y las salidas se producen por evaporación, por lo que las sales permanecen en el sistema, incrementándose poco a poco la salinidad del agua de la laguna. El incremento de CE detectado al comienzo del estudio, y posterior descenso (Fig. 3) podría deberse al ascenso de una capa meromíctica, aunque esta hipótesis no ha sido aún contrastada en campo. Finalmente, se ha estimado el tamaño de la superficie mínima de alimentación (i.e. la cuenca hidrogeológica) a la laguna de Santa Olalla y al sistema completo (Dulce-Olalla-Pajas). Este cálculo se ha realizado asumiendo unas entradas subterráneas de 0,39 hm³ durante el periodo de estudio. Posteriormente, se han realizado balances de agua en el suelo para dicho periodo con diferentes valores de reserva útil. Para obtener las entradas citadas, y con una reserva útil entre 60 y 75 mm (Guardiola, C, com. pers.), la cuenca hidrogeológica del sistema Dulce-Olalla-Pajas tiene, al menos, una extensión superficial entre 2200 y 6300 has. Es decir, la cuenca hidrogeológica es sensiblemente mayor que la superficial (500 has). Por lo tanto, es de vital importancia continuar con la supervisión y el control de las extracciones de aguas subterráneas y monitorizar de manera continua los niveles piezométricos en el entorno de la laguna, tanto los niveles someros como los profundos.

II.1.5. Conclusiones

El balance hídrico a escala diaria realizado en la laguna de Santa Olalla pone

de manifiesto una importante contribución de flujos subterráneos en la alimentación de la laguna (78%, frente al 22% de entradas por precipitación directa). Las principales salidas se producen por evaporación, salvo durante cortos episodios de intensas precipitaciones en los que la laguna recarga al acuífero. Las aguas son salobres y los niveles en piezómetros someros cercanos se mantuvieron sobre el nivel de agua de la laguna, lo que confirma los resultados obtenidos en el balance hídrico.

Agradecimientos

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II.2: Estimation of hydrogeological parameters by tidal influence methods in the recharge area of the sand aquifer in Doñana National Park (Huelva, Spain)

Cálculo de parámetros hidrogeológicos mediante métodos de influencia mareal en el acuífero de arenas de Doñana (Huelva, España).

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ABSTRACT

Through hourly monitoring of piezometric levels near Santa Olalla pond (Doñana Biological Reserve) tidal oscillations have been detected in two of the installed piezometers. The Doñana aquifer, which partly discharges into the ponds of the Doñana Biological Reserve, is a coastal aquifer. The tidal oscillation observed has been used to estimate values of transmissivity and permeability through the methods of tidal delay and tidal efficiency factor. Results obtained are within the values of hydrogeological parameters previously estimated for this area through traditional methods such as pumping tests.

Key-words: Tidal efficiency method, time lag method, coastal aquifer, transmissivity.

RESUMEN

A través de la monitorización horaria de niveles piezométricos próximos a la laguna de Santa Olalla (Reserva Biológica de Doñana) se han detectado oscilaciones mareales en dos de los piezómetros instalados. El acuífero de Doñana, el cual descarga en parte en las lagunas de la Reserva Biológica de Doñana, es un acuífero costero. Las oscilaciones mareales observadas nos han permitido estimar valores de transmisividad y permeabilidad en la zona de estudio a través de los métodos de retraso de marea y de eficiencia de mareas. Los resultados obtenidos se encuentran en el rango de los estimados previamente para esta zona con otros métodos como ensayos de bombeo.

Palabras clave: Método de eficiencia de marea, método de retraso de mareas, acuífero costero, transmisividad.

Geogaceta, 64 (2018), 51-54

II. 2.1. Introducción

El acuífero de Doñana ocupa una superficie de 2,600 km². Está dominado por depósitos de gravas y arenas del periodo plio-cuaternario que se extienden por las provincias andaluzas de Huelva, Sevilla y Cádiz (De Castro y Reinoso, 1997). En este trabajo nos centraremos en la Masa de Agua Subterránea Manto Eólico Litoral de Doñana (05.51.04), anteriormente denominado acuífero dunar (Vela, 1984) o acuífero de

arenas, la cual abarca una superficie de unos 90 km² desde el Océano Atlántico hasta el área de marismas del Parque Nacional de Doñana. Esta sub-unidad hidrogeológica es de tipología libre. Las proximidades de la laguna de Santa Olalla se caracterizan por estar formadas por una matriz arenosa de más de 130 metros de profundidad y una capa de arcillas entre los 93 y los 123 metros de profundidad (Salvany *et al.* 2010) (Fig. 1-B). Un basamento de margas miocenas constituye el muro del acuífero.



Fig. 1.- A) Ubicación de los piezómetros monitorizados en las proximidades de las lagunas Dulce y Santa Olalla, en un entorno de arenas estabilizadas y a tan solo 2,5 km del Océano Atlántico. En el margen superior derecho se muestra la localización del mareógrafo del cual se han obtenido los datos mareales. B) Columna litológica de un sondeo profundo ubicado en el entorno de Santa Olalla y que sirve de referencia para entender la litología de la zona (modificado de Salvany et al. 2010).

Fig. 1.- A) *Location of the monitored piezometers in the proximity of Dulce and Santa Olalla ponds, only 2.5 km from the Atlantic Ocean. The location of the tide gauge from which tidal data have been obtained is shown in the upper right corner. B) Lithological column of a deep piezometer located in the surroundings of the Santa Olalla pond (modified from Salvany et al. 2010).*

El Parque Nacional de Doñana (1080 km²), en el cual está incluida la Reserva Biológica de Doñana, se encuentra situado dentro de los límites del mencionado acuífero de Doñana. Nuestra zona de estudio se sitúa en el entorno de las lagunas de las arenas estabilizadas de la Reserva Biológica, a las cuales descarga el acuífero dunar. Otras salidas de agua del acuífero de mayor envergadura son las que se producen hacia el océano, así como el agua transpirada por la vegetación freatofítica (Muñoz -Reinoso, 2001). La laguna de Santa Olalla, la única de carácter permanente de este conjunto, se sitúa a 2,5 km de la costa. Esta y otras lagunas de tipo estacional del mismo entorno se están estudiando en la actualidad desde el punto de vista hidrogeológico con el objetivo de mejorar el conocimiento existente entre las aguas superficiales y las aguas subterráneas en esta zona. De forma indirecta, se pretende establecer si la presión antrópica sobre el acuífero por los bombeos de agua subterránea, tanto para abastecimiento en la urbanización costera de

Matalascañas, como para fines agrícolas en zonas más alejadas, puede tener repercusiones en el mantenimiento de nivel de agua en las lagunas estudiadas. Con estos objetivos se han instalado una serie de sensores, tanto en piezómetros de entre 20 y 2 m de profundidad, como en lagunas, para monitorizar a escala trihoraria las evoluciones del nivel existentes y en consecuencia las relaciones aguas superficiales-aguas subterráneas. En concreto, para este estudio, se han utilizado dos sensores instalados en piezómetros de la Confederación Hidrográfica del Guadalquivir (CHG) (Fig. 1A). En dichos sensores se han detectado oscilaciones que responden a la influencia de las mareas. Esta circunstancia ha permitido aplicar los métodos de retraso de mareas (R) y eficiencia de mareas (EM) para estimar los parámetros hidráulicos de transmisividad (T) y permeabilidad (K) con un coeficiente de almacenamiento (S) dado. Este tipo de metodologías, poco empleadas, pero utilizadas ampliamente por diversos autores desde los años 50 (e.g., Ferris, 1951; Carr y

Van Der Kamp, 1969) sirven como complemento de tecnologías más clásicas empleadas con el mismo fin.

II.2.2. Metodología

Los puntos denominados como PDUL y PSOLW, de 21 y 17 m de profundidad respectivamente, y situados a una distancia de 2500 y 2700 m del Océano Atlántico, han sido los utilizados para aplicar las metodologías de R y EM. Ambos sensores fueron programados para medir de forma horaria las oscilaciones del nivel piezométrico durante dos semanas (28/11/2017- 13/12/2017). Las medidas tomadas por estos sensores denominados Diver® han sido compensadas barométricamente para obtener valores finales de nivel piezométrico y corregidas en caso de errores puntuales. Mediante el acceso a la web de Puertos del Estado (www.portus.es) se han obtenido los datos necesarios para la comparación de los niveles piezométricos con el nivel del mar. Se han empleado los valores de nivel del mar registrados por el mareógrafo de Bonanza 2, situado en la desembocadura del río Guadalquivir (Cádiz) como nivel de referencia, por ser aquel que se encuentra más próximo (24 km) a nuestra zona de estudio (Fig. 1A). Se ha empleado un periodo de tiempo de tres días, desde el 7 de diciembre de 2017 a las 00:00 h hasta el 9 de diciembre a las 23:00 h del mismo año, con intervalos horarios. Durante este intervalo de tiempo no se registraron precipitaciones.

La estimación de los parámetros hidráulicos de transmisividad y permeabilidad en función de los datos de marea se ha llevado a cabo aplicando las ecuaciones del modelo de respuesta a las mareas desarrolladas por Sánchez-Úbeda *et al.* (2012) y aplicadas por Sánchez Úbeda *et al.* (2013) y Nieto-López *et al.* (2016). Dichas ecuaciones son:

A) Retardo de la oscilación del nivel piezométrico respecto a la oscilación de las mareas:

$$R = \frac{x}{2} \sqrt{\frac{t_0 S}{\pi T}} \quad (1)$$

donde R es el retardo o lag (horas) que se produce entre la señal de marea y la del nivel piezométrico, x es la distancia del punto a la línea de costa (en metros), y t₀ es el periodo de oscilación de la marea (12,5 horas). El valor de transmisividad se obtiene a través de valores de coeficiente de almacenamiento (S) dados.

B) Eficiencia de mareas

$$EM = \exp\left(-\sqrt{\frac{\pi x^2 S}{t_0 T}}\right) \quad (2)$$

El valor de EM es el cociente entre la amplitud de la oscilación del nivel piezométrico y la amplitud de mareas. Los valores de amplitud de la oscilación del nivel piezométrico y de las mareas se han obtenido mediante el método de amplitud media (Jha *et al.* 2003), calculando los valores medios de amplitud entre los máximos y mínimos correlativos en el periodo de estudio. A partir de los valores de transmisividad, se han calculado la permeabilidad ($K=T/b$, siendo b el espesor saturado).

Estas expresiones se desarrollaron para condiciones confinantes (Ferris, 1951), no obstante, se pueden aplicar a nuestro caso de acuífero libre cuando la razón entre la fluctuación del nivel piezométrico y el espesor saturado es menor a 0,02 (Roscoe Moss, 1990).

II.2.3. Resultados y discusión

Tal y como se observa en la figura 2, la influencia mareal es indiscutible en los piezómetros del área estudiada. Se distingue cómo las variaciones de nivel piezométrico comparten el mismo periodo que las oscilaciones mareales (12,5 horas). Asimismo, se puede observar la diferencia de orden entre la amplitud de los niveles piezométricos de PSOLW y PDUL, de 0,029 m y 0,031 m respectivamente y la amplitud

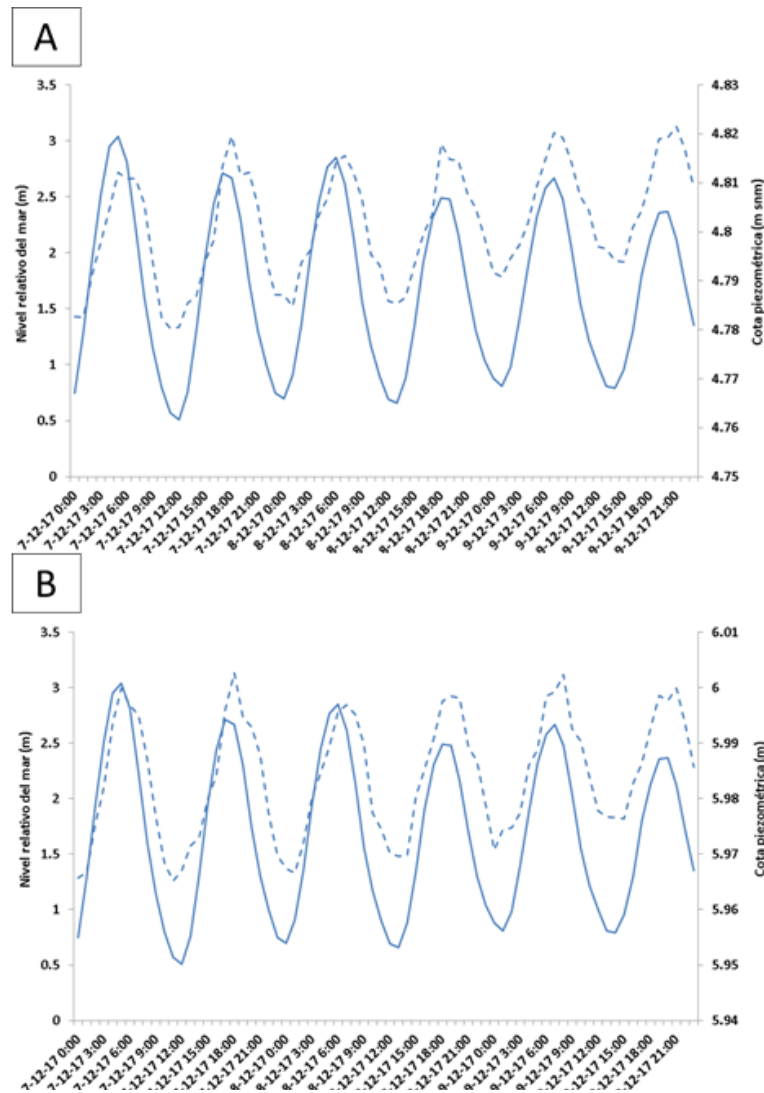


Fig. 2.- Registro de nivel relativo del mar y del nivel piezométrico en PSOLW (A) y PDUL (B), respectivamente, del 07-12-2017 a las 00:00 horas al 09-12-2017 a las 23:00 horas con una resolución horaria

Fig. 2.- Relative sea level and water table dataset in PSOLW (A) y PDUL (B) from 2017-12-07 at 00:00 h to 2017-12-09 at 23.00 h, at hourly intervals.

mareal en este punto del Océano Atlántico, de 2,2 m de media.

Se ha considerado que el retardo entre las mareas y PSOLW y PDUL (13,16 h y 13,35 h respectivamente) no corresponde a la pleamar directamente anterior, sino que, dada la distancia entre los puntos y la costa y tomando como referencia valores anteriores, el retardo sería atribuible a la marea que precede a la anterior (es decir 12,5 horas antes).

Este valor se podría afinar en un futuro si tuviese lugar alguna marea especialmente

significativa que produjese una respuesta identificable en los niveles piezométricos medidos.

Los valores de coeficiente de almacenamiento (S) empleados para el cálculo de T y K , han sido 0,01 y 0,001 (Sánchez Úbeda *et al.* 2013).

En ensayos de bombeo anteriores en la zona se estimaron valores incluso más bajos de S , de entre $2 \cdot 10^{-4}$ y $2 \cdot 10^{-3}$ en los primeros metros del acuífero, (IGME, 1992).

Tabla I: Valores de Transmisividad (T) y permeabilidad (K) calculados mediante los métodos de retraso de mareas (R) y de eficiencia de mareas (EM) para cada punto estudiado. “ np ” se utiliza como acrónimo de “nivel piezométrico”.

Table I: Transmissivity (T) and permeability (K) values calculated according to the methods of time lag (R) and tidal efficiency factor (EM) in the studied points. “ np ” is referred to “piezometric level”

						Método R		Método EM		
Punto	x (m)	Amplitud mareas (m)	Amplitud np (m)	Retardo (h)	EM	S	T (m²/d)	K (m/d)	T (m²/d)	k (m/d)
PSOLW	2.690	2,2	0,029	13,16	0,013	0,001	997	10	2329	23
						0,01	9975	95	23291	230
PDUL	2.573	2,2	0,031	13,35	0,014	0,001	900	9	2198	22
						0,01	9002	90	21981	220

Los valores de T obtenidos por la aplicación de ambos métodos se muestran en la tabla I. Se observa cómo los resultados obtenidos dependen fundamentalmente de los valores de S que se han otorgado para cada caso. Del mismo modo, se distinguen diferencias de un orden de magnitud entre los resultados de T obtenidos mediante el método de R (900 y 9975 m²/d) y el método de EM (2,329 – 23,291 m²/d), lo cual se ha observado también en otros trabajos mencionados anteriormente (Sánchez-Úbeda *et al.* 2013, Nieto-López *et al.* 2016). El valor de espesor saturado utilizado en el cálculo de la permeabilidad, a partir de los valores de transmisividad obtenidos, ha sido de 100 metros, ya que se trata de un valor medio del espesor del acuífero libre formado por arenas, mostrado en la figura 2. Los valores de K varían entre 9 m/d y 250 m/d.

Los valores de T y K de bibliografía para esta zona de estudio son muy diversos, ya que existen algunos autores que separan el acuífero de arenas en una unidad inferior y una superior separadas por una capa de arcillas de 30 metros de potencia y le otorgan parámetros diferentes a cada una de ellas (Lozano, 2007). Los resultados de transmisividad obtenidos en este trabajo están dentro de los 100 m²/día y 3000 m²/día, propuestos por el IGME (1992), y son de menor orden de magnitud que los obtenidos en otros acuíferos costeros

(Sánchez-Úbeda *et al.* 2013, Nieto-López *et al.* 2016). Los valores de K del rango más bajo calculados por los métodos de R y EM están dentro de los expuestos por Guardiola-Albert *et al.* (2010) de entre 0,001 m/d y 30 m/d para el acuífero.

Por otro lado, oscilaciones en el nivel piezométrico de menos de 1 cm de amplitud fueron detectadas en 1995 en un piezómetro próximo al palacio de Doñana, a 5800 metros de la costa (Olías-Álvarez, 1995). La diferencia entre esta amplitud y la detectada por nuestros sensores, indicaría que la señal de la marea se atenúa a medida que aumenta la distancia a la costa.

II.2.4. Conclusiones

La influencia de la oscilación de la marea ha sido detectada en dos piezómetros situados a escasos metros de distancia de la laguna de Santa Olalla (Reserva Biológica de Doñana) y a menos de 3 km del Océano Atlántico.

Los valores de transmisividad (T) y permeabilidad (K) obtenidos mediante los métodos de Retraso (R) y Eficiencia de Mareas (EM) difieren considerablemente, debido a la sensibilidad de cada método a los valores de coeficiente de almacenamiento y retardo de mareas. El método R arroja

resultados más similares a los estimados en estudios previos, por tanto, se considera el más adecuado para la estimación de estos parámetros hidráulicos, al menos para la subunidad hidrogeológica del acuífero dunar, objeto del presente estudio. Por otro lado, los valores obtenidos de T (cercaos a 900 m²/día) y K (cercaos a 10 m²/día) con el parámetro S igual a 0,001 son similares a los estimados por otros autores en la misma zona de estudio.

Mediante este tipo de métodos, es posible establecer valores de conductividad hidráulica representativos de la zona existente entre el piezómetro y la costa en lugar de datos puntuales, como arrojan los ensayos de bombeo, técnica empleada habitualmente.

Agradecimientos

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II.3: Assessment of the hydrological status of Doñana dune ponds: a natural World Heritage Site under threat.

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ABSTRACT

The hydrological response of shallow ponds to groundwater withdrawal has been of growing concern in the Doñana National Park (southern Spain) in recent decades. This study examines the role of groundwater in maintaining the hydroperiod (i.e. the hydrological regime) in the park's main dune ponds, by quantifying the groundwater fluxes to/from them. The hydrological characterization was performed by applying different methodologies. Daily hydrological balances registered in the ponds revealed groundwater contributions ranging from 80% of the total water inflows (i.e. groundwater discharge) to a net groundwater recharge from the ponds to the aquifer, and enabled the studied water bodies to be classified as discharge or recharge systems. The recharge systems must have been influenced by the lowering of piezometric levels due to groundwater extraction for urban supply in a nearby coastal resort.

Keywords: *surface water–groundwater interaction; water balance; Doñana Biological Reserve; hydrochemistry; sand dune pond.*

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II.3.1. Introduction

The demand for fresh groundwater is especially significant in arid regions (Kundzewicz and Doell 2009), including Spain, which is the most arid country in Europe (Llamas 2003). Groundwater demand for different uses has increased rapidly over the past four decades. This increase results in conflicts between wetlands conservation and groundwater exploitation.

Even though the majority of the most significant wetlands at an international level are protected, they are still endangered by a range of pressures (Scheffer *et al.* 2015). Severe degradation of numerous important wetlands, such as mangroves (Sakho *et al.* 2011, Jaramillo *et al.* 2018) or dune slacks (Geelen *et al.* 2017), has been caused by, for example, modification of hydrological connectivity, groundwater withdrawal and surface water pollution (Green *et al.* 2017). In addition, climate change is widely expected to increase the stress on these and other wetlands, although

they are not jeopardized by any local stressor (Junk *et al.* 2013). Given the importance of wetlands in preserving landscape biodiversity, further research is necessary. Their richness and diversity may to some extent be linked to their basin characteristics, as they are sinks for substances draining from their catchments and typically reflect local natural variations in geology, hydrology and plant communities (Rodríguez-Rodríguez, 2007). The conservation of Doñana National Park (DNP) is particularly challenging, requiring coordinated action between water authorities and stakeholders (Maltby and Acreman, 2011).

The coastal sector of the DNP consists of a major deposit of aeolian sands, including both a mobile and a stabilized dune system. These sands contain more than three thousand ponds, the majority of them flooded only after rainy periods (Green *et al.* 2016). The DNP contains a large seasonal marsh formed by the siltation of the former Guadalquivir River Delta. The originally tidal marsh is no longer influenced by the sea. In addition, more than three-quarters

of the original marsh has been modified by human activities since the beginning the 20th century, mostly for the development of new rice crop agriculture in this part of Spain. The area has been granted protected status since 1969 when it was declared a National Park. Later on, it was designated a Wetland of International Importance by the Ramsar Convention in 1982, a Special Protection Area for birds in 1988, and a natural World Heritage Site by the United Nations Educational Scientific and Cultural Organization (UNESCO) Convention in 1994. In recent years, there have been controversies due to the fact that the Doñana wetlands could be classed as being “in danger” by UNESCO if the Spanish authorities do not take the proper measures to solve a number of potential threats to the National Park: impacts from infrastructural projects such as a gas storage facility, the re-opening of the Aznalcollar mine upstream, unsustainable groundwater extractions, and the Guadalquivir River dredging project (UNESCO, 2017). If this new classification comes to pass, Spain could be the first EU country with a National Park listed as being “in danger”. Water for irrigation and human consumption is being taken out of the aquifer. Groundwater extraction for irrigation totals $60\text{--}90 \times 10^6 \text{ m}^3$ per year. Extractions for urban water supply are in excess of $2.75 \times 10^6 \text{ m}^3$ per year in a nearby coastal resort located on the southwest border of the park (Dimitriou *et al.* 2017).

With respect to the marshes, the “Doñana 2005” plan was implemented after a mining accident in a nearby town (Aznalcollar), outside the limits of the National Park, which had devastating consequences for the entire ecosystem. It involved the restoration of the marshes as well as improvement of the quantity and quality of water from the streams entering the wetland (Meharg *et al.* 1999).

Regarding the sand dune ponds, these ecosystems are of remarkable singularity in Europe, due to the fact that they are a biologically important habitat, renowned both for their specialized assemblages among

aquatic organisms such as macroinvertebrates and for the considerable number of rare and endemic species they sustain (Serrano *et al.* 2008). The protection of these ecosystems became an international issue in 1990. Even during the fourth meeting of the Ramsar Convention, the risk of ecological changes, such as the disappearance of some of the ponds and the loss of streams, was highlighted by Suso and Llamas (1993). Even though the aquifer of the stabilized dunes is mainly formed by sands, there are also less permeable deposits – clays and organic silt – at different depths in the deepest parts of the dune slacks, which contribute to the hydrogeological complexity of this system (Custodio *et al.* 2009). The formation of temporary ponds in certain areas is, therefore, conditioned by local groundwater discharge sectors of the aquifer and, probably, by the presence of low permeability materials at depth. The hydrogeological literature published about the hydrology of the Doñana coastal wetlands has highlighted that the ponds which show an anthropogenic alteration of the hydrological regime, or hydroperiod, are the ones located nearest to the abovementioned coastal resort, where declines in piezometric levels are sharper (e.g. Charco del Toro pond, Fig. 1). This effect was shown by Olías Álvarez and Rodríguez-Rodríguez (2013), who found that, from 1992 to 2012, the most drastic declines in piezometric levels were located in the surroundings of the irrigated cropland, reaching more than 6 m in deep piezometers.

The leading objective of this study is to achieve better knowledge of the groundwater–surface water interactions in some of the ponds located in the DNP. Partial objectives involve: (1) assessing the possible hydrological impact on the temporary ponds due to groundwater withdrawal in nearby areas by analysing daily piezometric tendencies over a period of almost four years (2013–2016); and (2) studying the hydrological functioning of the main ponds in the area by means of daily water balances, piezometric analysis and surface and groundwater hydrochemistry.

II.3.2. Study site

The Doñana aquifer (Fig. 1(a)) covers more than 2,500 km², in the mouth of a 57,000-km² basin (the Guadalquivir River basin). Its thickness is between 10 m in the north and more than 200 m at the southern coastal border. The impervious materials that underlie the aquifer are marls of Miocene age (Custodio *et al.* 1992). The aquifer is divided into two sectors: confined (marshland) and unconfined (conglomerates and sands). The hydraulic parameters of the materials vary from north to south. Transmissivity ranges from 10^{-4} to 10^{-2} m²/s near the coast. In addition, the storage

coefficient varies between 5×10^{-4} in the marshland and 3×10^{-2} in the unconfined part. The ponds studied sit over the unconfined aquifer, classified by Vela (1984) as a “dune aquifer”, which has a surface area of 90 km² and stretches from the Atlantic Ocean to the marshes. It receives direct recharge from rainfall and it is made up mainly of permeable aeolian sands (Fig. 1(a)), with the presence of lenticular bodies of silt and clay. The water table is very close to the surface, at between 1 and 10 m below ground level (Olías *et al.* 2008). The aeolian sands overlie a deeper and more permeable layer comprised of coarser materials of fluvio-deltaic origin (Custodio *et*

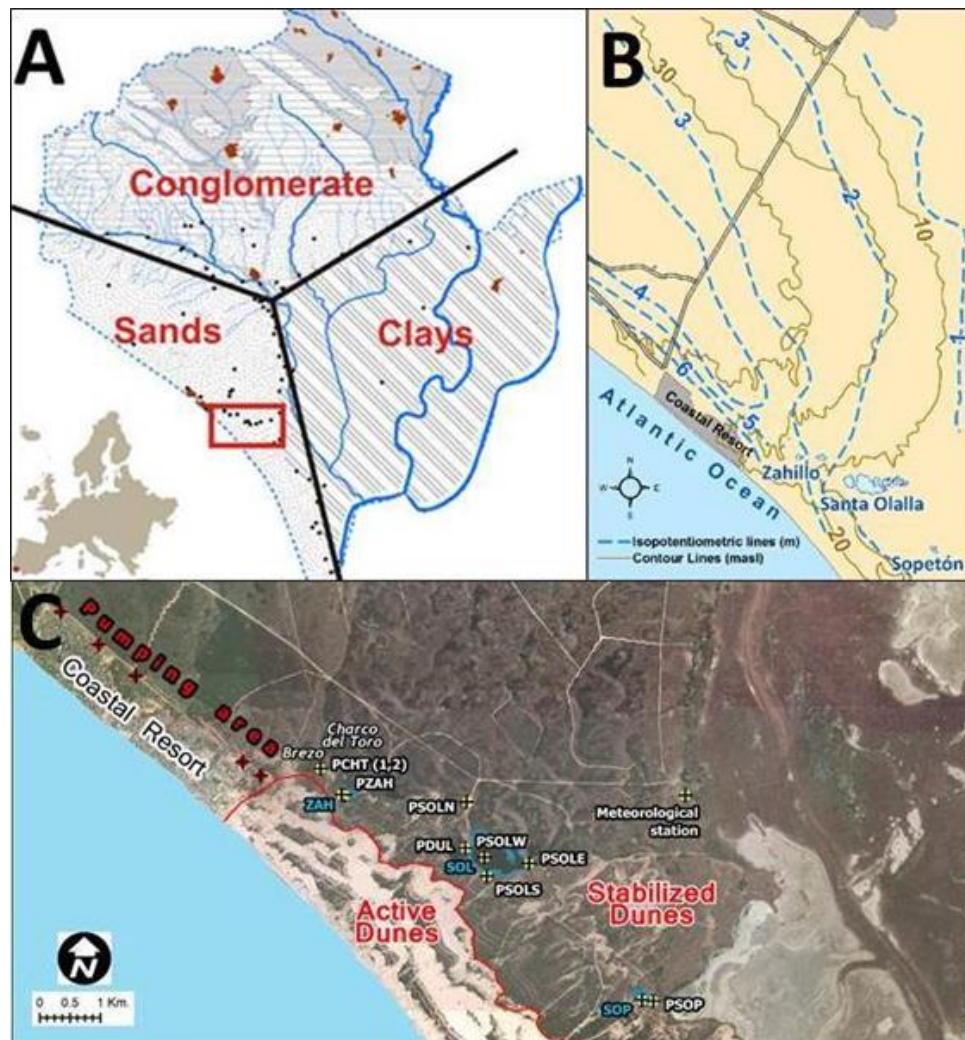


Figure 1. (a) Doñana aquifer and location of the Doñana National Park in Europe. (b) Isopotentiometric map of the eastern part of the dune aquifer (modified from Lozano-Tomás 2007). (c) Location of the study area and the pumping site of the coastal resort. The Charco del Toro, Zahillo (ZAH), Santa Olalla (SOL) and Sopotón (SOP) ponds are marked. Palacio de Doñana meteorological station can also be seen. All of these ponds and sensors are located over the stabilized dunes. P: piezometers.

*al.*1992). All the aquatic ecosystems (rivers, seasonal and permanent ponds, etc.) in the DNP rely on groundwater inputs from the aquifer (De Castro and Muñoz-Reinoso, 1997). As explained above, groundwater withdrawal of more than $60 \times 10^6 \text{ m}^3$ by wells, hundreds of them illegal, has had a hydrological impact in some zones. Furthermore, there are several signs of alterations, such as changes in vegetation and a drop in the water levels in the ponds near a coastal resort due to pumping activity (Serrano and Serrano, 1996; Muñoz-Reinoso, 2001; Serrano and Zunzunegui 2008; Manzano *et al.* 2009; Custodio, 2010). The total disappearance of two sand dune ponds strengthens the evidence for this. Nearest to the coastal resort, the Brezo pond has been dry since 1976 (Hollis *et al.* 1989) and the Charco del Toro pond (Fig. 1(c)) has been dry since 2010 (Díaz-Paniagua and Aragones, 2015).

This research focuses on three ponds located in the Doñana Biological Reserve. This reserve (6800 ha) is located within the boundaries of the DNP and enjoys the highest level of conservation status amongst the Doñana Protected Areas. Activities in the area are restricted to scientific research and the implementation of wildlife conservation programs. The ponds are located on the west side of the reserve, over stabilized and vegetated dunes (Fig. 1). The distance from the study area to the Atlantic Ocean is up to 2 km.

Figure 1 shows the Doñana aquifer and the location of the Matalascañas coastal resort, as well as the study zone with the location of the Brezo, Charco del Toro, Zahillo, Santa Olalla and Sopotón ponds. The location of the piezometers is also shown. The last three ponds are the subject of this study, referred to henceforth by the abbreviations ZAH, SOL and SOP, respectively.

The climate in the study area is Mediterranean, classified as dry sub-humid with Atlantic influences, characterized by a high inter- and intra-annual variability (Florencio *et al.* 2009). The dry season lasts from April to September. The annual average

rainfall is between 500 and 600 mm (Dimitriou *et al.* 2017). The annual potential evapotranspiration is estimated to be 900 mm and free surface evaporation 1500 mm (Suso and Llamas 1993). Mean monthly temperatures are about 25°C in July and 10°C in January.

The Doñana aquifer has an estimated annual recharge of $174 \times 10^6 \text{ m}^3$ coming from the direct infiltration of precipitation in the unconfined part of the aquifer (IGME, 2007). Discharge goes mainly to the sea via the sand dune aquifer, to the main watercourses, to the marshlands and, finally, to the ponds, which are the main groundwater-dependent ecosystems in the area. The damping effect of groundwater discharge is vital for the maintenance of these ecosystems, since it provides a more continuous water input than that provided by rainfall.

II.3.3. Methodology

To conduct the water-level monitoring, sensors that measure the total pressure at a 3-h time interval (Diver, Level-logger and CTD-Decagon) were installed in each of the piezometers and ponds shown in Figure 1(c). Atmospheric pressure transducers were installed nearby to compensate for the measurements of the above-mentioned sensors. Also, measurements taken directly in the field were used to calibrate the automatic measurements of the sensors.

A conceptual model (Fig. 2) developed by Rodríguez-Rodríguez *et al.* (2016) was followed to define the components of the hydrological budget in the ZAH, SOL and SOP ponds. Groundwater net flux (GWNF) was the unknown variable in the water balance equation:

$$\text{WNF} = E - P \pm \Delta S \quad (1)$$

where E is the direct evaporation from the water surface; P is direct precipitation; and ΔS is the change in the water stored.

II. Hydrodynamic methods

Data obtained from weather stations (Fig. 1) were used to estimate both water inputs (P) and outputs (E). Water outputs were estimated following the best method to calculate losses by evaporation from shallow water bodies (McMahon *et al.* 2013). This method is based on the original Penman formula (Penman, 1956), which is a semi-empirical equation combining mass transfer and energy budget methods. Variables needed to calculate E are air temperature, relative humidity, solar radiation and wind speed, as well as other parameters. Such data were obtained at a daily time step from the meteorological station located approximately 12 km to the north of the SOL pond (Fig. 1). Changes in the volume of water stored in the ponds (ΔS) were quantified using the hypsometric curve. The hypsometric curve of a pond relates the horizontal cross-sectional area of the pond basin to the water level recorded by sensors. The curves were estimated using the equation developed by Hayashi and Van der Kamp (2000), and were used to determine the surface of each of the ponds at a daily time step to calculate the volume and ascertain the variation in storage in each pond.

No streams or ephemeral creeks are found in the area. Given the high permeability of the sands, surface runoff does not need to be accounted for in the water balance equation.

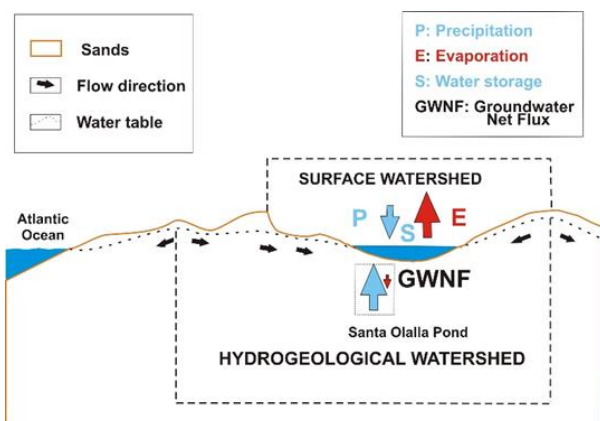


Figure 2. Hydrological sketch of the Santa Olalla pond and its relation to the coastal aquifer.

The water balance calculations for the three ponds were carried out between December 2016 and June 2017 and from February to June 2018, adapted to the flooding period of the ZAH pond. Equation (2) gives an estimation of hydraulic gradients (HG) from piezometers close to the SOL pond:

$$HG = (\Delta h / \Delta x) \quad (2)$$

where Δh is the difference between the daily water table of each piezometer and the water level in the SOL pond (in m a.s.l.); and Δx is the distance from each piezometer to the pond.

The piezometers used to calculate the hydraulic gradient (see Fig. 1), are: PSOLN (3.5 m deep), PSOLE (2.7 m deep), PSOLS (2.7 m deep) and PSOLW (17.2 m deep).

The hydrochemical facies of the water samples were obtained with a Dionex ICS-1000 ionic chromatograph. Bicarbonate analysis was carried out by means of colourimetry. Hydrochemical data for the period April 2016–May 2018 were processed using AquaChem software (Waterloo Hydrogeologic).

II.3.4. Results

The basic hydrological and morphometric characteristics of the ponds studied are given in Table 1. The values for salinity and water depth correspond to the year 2016.

Piezometric levels measured between 2013 and 2016 are shown in Figure 3. The variations in two close piezometers located in the Charco del Toro area, (PCHT1, close to the pond bed, and PCHT2, on the pond bed; both less than 1 km away from the coastal resort) were compared with those observed in the PSOLE piezometer, around 4.6 km away from the resort (Fig. 1) and the cumulative deviation of the rainfall (CDR). Slopes of the linear variations obtained in the time series were negative. Nevertheless, the slope of PSOLE (-9×10^{-5}) is smaller than those of PCHT1 (-5×10^{-4}) and PCHT2 (-7×10^{-4}). A linear

II. Hydrodynamic methods

Table 1. Hydrological and morphometric indexes of the ponds studied. AFS: average flooded surface; WS: watershed surface.

	AFS (ha)	WS (ha)	Sal. (g/l)	Max. Water Depth (m)	Min. Water Depth (m)	Height (m asl)
Santa Olalla	25	155	3-16.6	2.1	1.3	3.4
Zahillo	4.8	36	0.3-0.5	0.4	0	7.6
Sopetón	2.3	38	1.3-1.7	0.7	0	1.8

regression model was made for the slopes of the piezometer values and also for the slope of the CDR rainfall time series. The results show that, for PCHT1 and PCHT2, there is a very significant decreasing trend of the piezometric time series evolution ($p = 2.2 \times 10^{-16}$ in both cases), whereas for PSOLE and CDR, the trends were found to be not significant ($p =$

The results of the water balance in the ZAH, SOL and SOP ponds (December 2016–June 2017 and February–June 2018, during which periods the ponds were flooded) are presented in Table 2. Daily water inputs (rainfall) and outputs (evaporation), as well as the variation in storage (ΔS) are shown. The GWNF was calculated from Equation (1). In

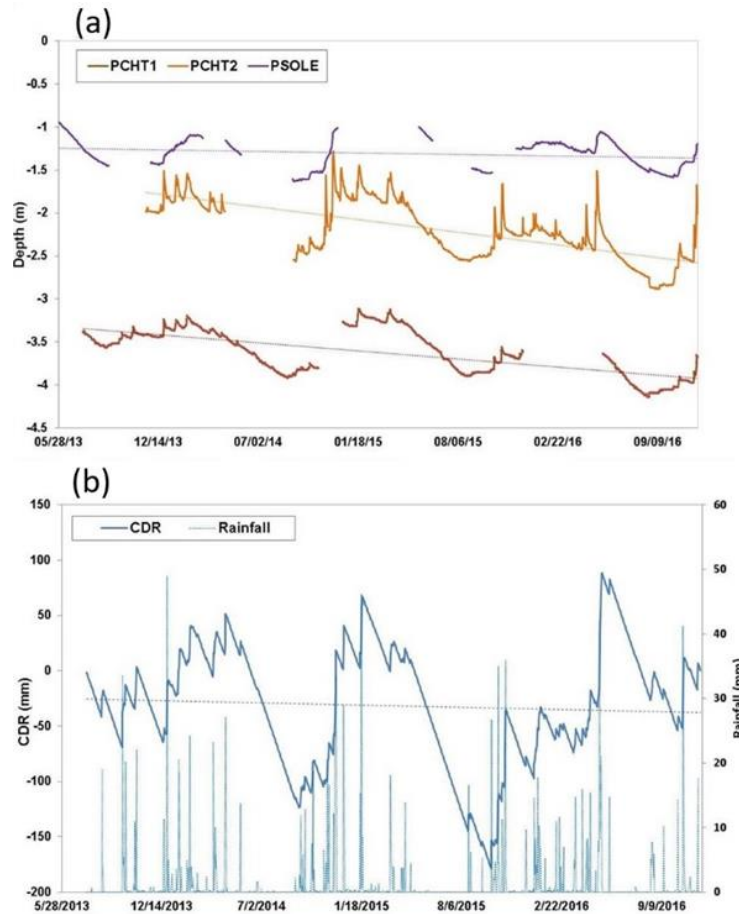


Figure 3. (a) Water table evolution over four years in three piezometers (data provided by the Guadalquivir River Basin Authority). (b) Daily rainfall values and cumulative deviation of the mean rainfall (CDR) for the same time period. Trend lines are drawn in all cases.

Table 2. Water balance in the Zahíllo, Santa Olalla and Sopetón ponds: (a) 3 December 2016–14 June 2017 and (b) 28 February–20 June 2018. GWNF: groundwater net flux; negative values of GWNF are considered to be water outputs from the pond to the aquifer, i.e.

A)	ZAHÍLLO	Rainfall	GWNF	Evaporation	ΔS
	Total (mm)	301	426	743	-16
	Daily Max. (mm/day)	39.2	208	8.9	206
	Daily Min. (mm/day)	0	-44	0.8	-32
	Daily Average (mm/day)	1.5	2.2	3.8	-0.1
	Daily Median (mm/day)	0	0.25	3.2	-3.2
	SANTA OLALLA	Rainfall	GWNF	Evaporation	ΔS
	Total (mm)	301	890	743	448
	Daily Max. (mm/day)	39.2	142	8.9	147
	Daily Min. (mm/day)	0	-37	0.8	-19
	Daily Average (mm/day)	1.5	4.6	3.8	2.3
	Daily Median (mm/day)	0	2.25	3.2	-0.6
	SOPETÓN	Rainfall	GWNF	Evaporation	ΔS
	Total (mm)	301	511	743	69
	Daily Max. (mm/day)	39.2	57	8.9	55
	Daily Min. (mm/day)	0	-36	0.8	-29
	Daily Average (mm/day)	1.5	2.6	3.8	0.35
	Daily Median (mm/day)	0	2.56	3.2	-1.4
B)	ZAHILLO	Rainfall	GWNF	Evaporation	ΔS
	Total (mm)	320	326.9	562	84.6
	Daily Max. (mm/day)	39	74.5	9.2	110.25
	Daily Min. (mm/day)	0	-23.2	1.2	-11.6
	Daily Average (mm/day)	2.8	2.9	5	0.75
	Daily Median (mm/day)	0	-0.36	4.8	-4.25
	SANTA OLALLA	Rainfall	GWNF	Evaporation	ΔS
	Total (mm)	320	521.6	562	279.44
	Daily Max. (mm/day)	39	66.5	9.2	75.75
	Daily Min. (mm/day)	0	-34.5	1.2	-12.4
	Daily Average (mm/day)	2.8	4.6	5	2.5
	Daily Median (mm/day)	0	2.32	4.8	-2.6
	SOPETON	Rainfall	GWNF	Evaporation	ΔS
	Total (mm)	320	239.9	562	-2.12
	Daily Max. (mm/day)	39	44.4	9.2	39.12
	Daily Min. (mm/day)	0	-23.4	1.2	-22.5
	Daily Average (mm/day)	2.8	2.1	5	-0.02
	Daily Median (mm/day)	0	1.05	4.8	-3.12

ZAH, SOP and SOL was, respectively, -44 , -36 and -37 mm/d, in all cases after precipitation events. The total input due to direct rainfall in this period was 301 mm, while the total specific flow of GWNF was 426, 511 and 890 mm, respectively (Table 2). It must be emphasized that the median value of GWNF in ZAH (0.25 mm/d) differs by an order of magnitude from those of SOP and SOL (2.60 and 2.25 mm/d, respectively), which indicates a significant difference in their hydrological functioning. The main loss of water in all cases was by evaporation. The ΔS also demonstrates the hydrological tendencies in the ponds. While the total ΔS of the SOL and SOP ponds was positive, that of the ZAH pond was negative, which means that the overall tendency of the latter pond during the period was to decrease. In Table 2(b), which shows the water balances of the ZAH, SOL and SOP ponds for February–June 2018, total rainfall is similar to that for the first period (320 mm), although evaporation was higher in the first period (743 vs 562 mm). One of the main differences in this second

period is that daily median specific flow in ZAH pond was found to be negative (-0.36 mm/d), in contrast with those of SOL (2.32 mm/d) and SOP (1.05 mm/d). As for the other components of the water balance, values obtained for daily average, minimum and maximum were not very different from those found in the earlier period of the study.

The results of the hydraulic gradients calculated between the four piezometers (Fig. 1) and the SOL pond are presented in Figure 4, which shows that all hydraulic gradients had a positive value, meaning flows were from the piezometers to the pond. Piezometer PSOLS was found to have the highest hydraulic gradient to the SOL pond, while PSOLN had the lowest. This low gradient was due to the considerable distance – more than 600 m – between PSOLN and the SOL pond. Piezometers PSOLW and PSOLE showed similar variations, although some differences in their behaviour could also be observed. Piezometers PSOLE and PSOLS, which are shallower than PSOLW and PSOLN, showed

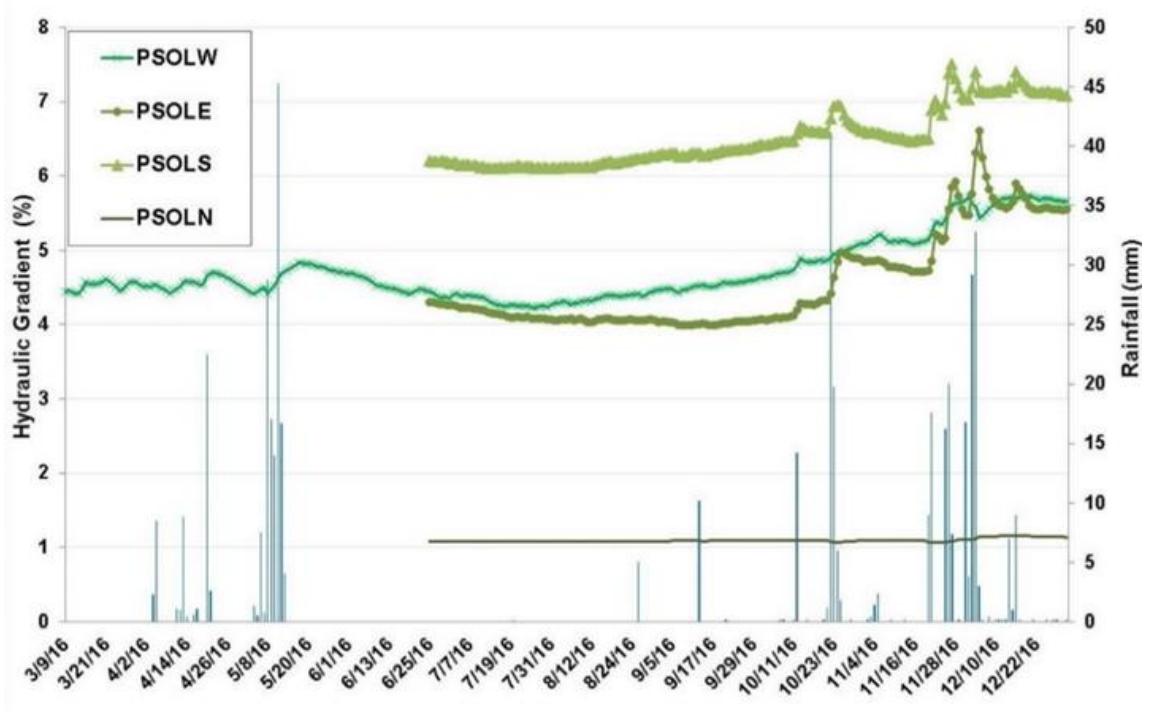


Figure 4. Daily values of hydraulic gradients towards the SOL pond and rainfall from March to December 2016.

sharp increases in their hydraulic gradient values when precipitation events took place.

Figure 5 shows the evolution of the piezometric level in the piezometers near the study ponds, as well as the evolution of the surface water during the period 24 June 2016–20 June 2018. The elevation of the pond bottom is also marked. The ZAH pond is located at the highest altitude (7.6 m a.s.l.), while the SOP pond is at the lowest altitude (1.8 m a.s.l.), as indicated in Table 1. The direct rainfall of the first year (June 2016–June 2017) was 533 mm, while a slightly higher value was registered in the second year (555 mm). In the period June 2017–June 2018, the main precipitation events occurred in late autumn and spring, starting a month later than in the first period. Water level measures in the ZAH pond were recorded in a shallow piezometer installed in the pond bed. This pond was flooded for 6 months (December 2016–June 2017) in the first year and for 4 months (March–June 2018) in the second year. The water level in the SOL pond decreased from the beginning of the study period to October 2016, when rainfall events occurred. The maximum water level (5.88 m a.s.l.) was

recorded in March 2017. Later, in May 2017, with the increase of the evaporation rate, water levels started to decline (the minimum value in 2017 was 4.62 m a.s.l.). In 2017, the levels started to increase again at the end of November, after a 3-day rainfall event with a total of 102 mm. Consequently, the maximum levels in this year (5.73 m a.s.l.) were reached a month later, at the end of April 2018.

As may be seen in Figure 5, the water table in piezometer PSOLW was above the water level in the SOL pond throughout the study period. Finally, the hydroperiod of the SOP pond lasted from November to the following June (7 months) in the first year and from the end of November to the following August (9 months) in the second year. The maximum records registered in both years were very similar (2.7 m a.s.l.). Piezometric levels near the SOP pond were a few centimetres lower than the altitude of the surface water of the pond.

Figure 6 presents the results of hydrochemical analysis in two Schöeller diagrams. Figure 6(a) shows the hydrochemical

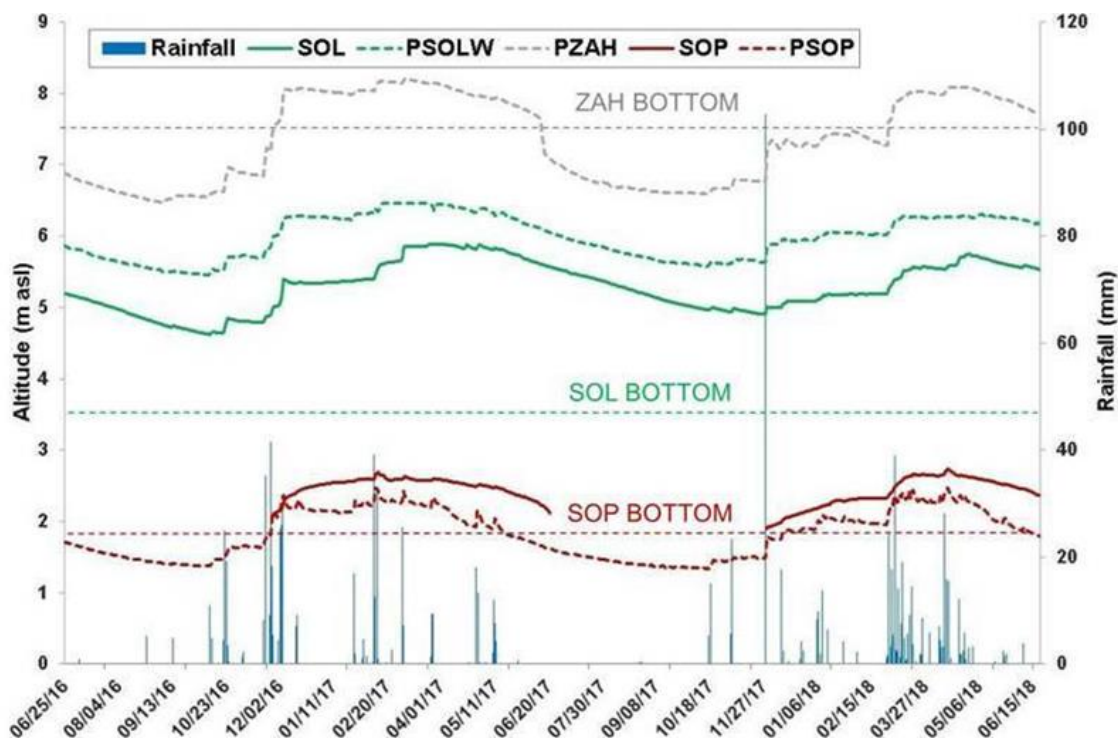


Figure 5. Water level and water table evolution in ponds and piezometers from June 2016 to June 2018.

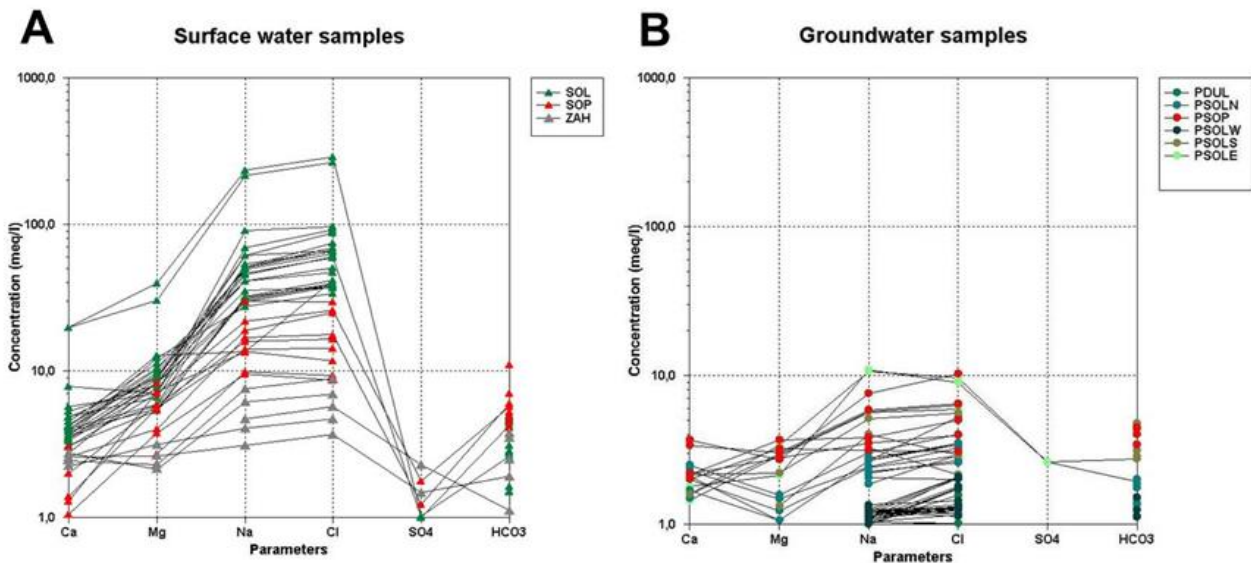


Figure 6. Schöeller diagrams of (a) surface water samples and (b) groundwater samples.

characteristics of surface water samples from the study ponds. A sodium-chloride-type facies was predominant, particularly in the SOL water samples, which registered chloride concentrations of between 30 and 300 meq/L, making it a brackishwater-type pond. The SOP pond exhibited chloride concentrations in the range 10–20 meq/L; however, the ZAH pond was found to be a freshwater system (Cl^- : 5–9 meq/L). Figure 6(b) shows the hydrochemical facies of the groundwater samples. The salinities of the groundwater samples were much lower than those of the surface water samples, varying from fresh to slightly brackish groundwater. The hydrochemical facies of the groundwater samples were of a mixed sodium-chloride type.

II.3.5. Discussion

In the proximity of the coastal resort, groundwater levels in the study piezometers declined more than 1 m. Custodio *et al.* (2009) recognized that, in some areas, piezometric levels had been decreasing since 1970, reducing groundwater discharge to dependent ecosystems. This effect has probably been caused by both the introduction of berry crops in the surrounding area and an increase in population in nearby towns. More recently, Dimitriou *et al.* (2017) showed the water level

decline in four temporary ponds in the Doñana coastal aquifer using a hydrodynamic numerical model.

The results of the estimation of groundwater net fluxes in the ZAH, SOL and SOP ponds during two flooded periods suggest that both the SOL and SOP ponds act as discharge ponds, as, in both cases, there were water inputs from the aquifer to the ponds. In the SOL pond, this behaviour was already stated by Sacks *et al.* (1992) and Lozano-Tomás (2007). In the SOP pond, the proximity of the marshes at a lower altitude incites regional groundwater fluxes towards them. This pond overflows towards the marshes during heavy floods, similar to other sand dune ponds in the area (Serrano *et al.* 2008).

However, the ZAH pond behaves as a recharge pond (i. e. the opposite process occurs). In previous studies carried out by the authors (Fernández-Ayuso *et al.* 2018) in the same ponds, the GWNF in three months (summer 2016) was estimated. The values obtained for SOL, SOP and ZAH were 2.4, 1 and -0.9 mm/d, respectively. As stated by Serrano and Serrano (1996), Serrano and Zunzunegui (2008), Manzano *et al.* (2009) and Dimitriou *et al.* (2017), the hydrological behaviour of the ZAH pond has already been

altered, and this alteration was most probably caused by groundwater pumping in the nearby coastal resort (more than $2.75 \times 10^6 \text{ m}^3/\text{year}$) and the consequent depletion of the piezometric levels below the pond, inducing recharge.

Furthermore, an increase in evaporation rates is expected due to climate change, as reported by Guardiola-Albert and Jackson (2011) and Scheffer *et al.* (2015). These researchers also stated that the aquifer recharge produced by precipitation would be reduced. This would lead to a decrease in groundwater input towards the ponds and other dependent ecosystems.

The hydraulic gradient values measured between the SOL pond and nearby piezometers were positive towards the pond. No flux inversion occurred during the study period. This situation has been detected in other Spanish wetlands with similar anthropogenic pressures, such as Las Tablas de Daimiel National Park (Castaño *et al.* 2018, Aguilera *et al.* 2013). The parallels between these two significant Spanish wetlands, both highly dependent on groundwater resources in terms of conflicts in water management, were stated internationally for the first time by Llamas (1988). Additionally, a progressive decay in groundwater levels due to water withdrawals is being observed in other protected wetlands in the Mediterranean region, resulting in deterioration in water quality and a loss of biodiversity (Green *et al.* 2017).

The stable hydroperiod in the SOL and SOP ponds and the reduction in flooded surface in the ZAH and Charco del Toro ponds can be observed in an application developed recently by the European Commission's Joint Research Centre (2016), Global Surface Water Explorer (<https://global-surface-water.appspot.com/>), which shows the extent and change of surface water bodies from 1984 to 2015.

A significant decreasing trend was clear in the PCHT1 and PCHT2 areas, whereas in piezometer PSOLE no significant decreasing trend could be observed. Comparing the rainfall

trend over the same period, it is obvious that this sector of the aquifer is being affected by some reductions at the aquifer recharge, mainly due to the withdrawal of the nearby groundwater resources. Otherwise, the trend in PCHT1 and PCHT2 would be similar to the evolution of rainfall in terms of cumulated deviation from the mean over this same period.

Concerning hydrochemistry, the high salinity of the SOL pond can be explained by the hydrological functioning of the system: inputs are from groundwater and rainwater with low salinity ($<0.2 \text{ g/l}$) and outputs are by evaporation, so the salts remain in the system, gradually increasing the salinity of the pond (Manzano *et al.* 2008). Furthermore, some of the SOL water inputs come from an adjacent pond, through local groundwater fluxes, which also contribute to its salt content. Salinity in the ZAH pond was much lower than in the other ponds, since water outputs were by evaporation, but also by infiltration from the pond towards the aquifer and, therefore, not all the salts remained in the pond. In view of the above, understanding the dynamic nature of groundwater–surface water interactions can be considered to facilitate the interpretation of hydrological and chemical relationships between the ponds and the groundwater (Sacks *et al.* 1992).

Taking all these facts into account, urgent action must be taken with regard to water management in the DNP, to preserve the remaining ponds not yet affected by local pressures.

II.3.6. Conclusions

This study has allowed us to improve existing knowledge of the hydrological functioning of three representative dune ponds located in the Doñana National Park, illustrating the scientific benefits of integrating both hydrological and hydrochemical tools in surface water–groundwater interaction studies. The groundwater hydrograms in piezometers not influenced by the pumping area in a nearby

coastal resort showed a similar trend to the cumulative evolution of precipitation. However, those piezometers located near to the coastal resort showed a remarkably higher slope in this trend. The results from the water balances carried out between 2016 and 2018 show that the Santa Olalla (SOL) pond is strongly dependent on groundwater discharge from the aquifer; threequarters of the water inputs come from such a source, with a median value of 2.3 mm/d. The main water output from the system was direct evaporation from the pond surface and small quantities of groundwater recharge during certain periods. The Sopetón (SOP) pond received median groundwater discharge of 1.8 mm/d, also behaving as a discharge pond. However, the Zahillo (ZAH) pond turned out to be a recharge pond; the median value of groundwater net flux was -0.1 mm/d for the period studied. The results of the water balance estimations and the decline in piezometric levels near Zahillo pond suggest that its proximity to the coastal resort has resulted in significant alterations to its hydrology.

The hydrochemistry results highlight the differences in hydrological regime between the ponds. Whereas the mean salinity of the water in the SOL and SOP ponds is of a brackish type, in the ZAH pond, the mean salinity is much lower. However, groundwater at the aquifer is freshwater and of a mixed sodium-chloride type. The hydrochemical facies of the surface water in the ponds is sodium chloride, indicating an intense evaporative mark in the hydrological functioning of the systems.

The outcomes of this study confirm that there is an alteration in the hydrology of the ZAH pond caused by groundwater withdrawal in nearby wells for urban supply. Moreover, the decreasing trend of the groundwater table in recent years, detected in the piezometers located between the pond and the pumping

area, supports this idea. A former pond (Charco del Toro) near these piezometers dried out permanently in 2010. This situation has not yet been detected in Santa Olalla, although its proximity to the extraction area is a direct pressure that has to be monitored carefully in the near future to avoid an irreversible alteration in this permanent pond.

Apart from hydrological changes due to direct human pressure, those triggered by climatic change must also be considered, as these would create the need to adopt additional measures. Efforts to improve knowledge of the hydrological functioning of these ponds would seem to be crucial when it comes to encouraging the authorities and stakeholders take action to protect them. Furthermore, responsibility for their protection does not fall solely within Spanish boundaries, since Doñana is currently a World Heritage Site.

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Chapter III: Thermal and hydrochemical methods



III.1: Using thermal modelling to characterize the groundwater discharge towards a permanent pond (Doñana National Park, Spain).

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ABSTRACT

The physical limnology of a shallow pond system was characterized using field measurements of water temperature, pH, and electrical conductivity (EC). We determined the spatial variability in surface and groundwater temperature, pH, and EC along the pond's shore and along the several pond-shore transects, analyzed the water column temperature gradient and estimated the groundwater discharge rate using a heat transfer model. The fieldwork was conducted in Santa Olalla and Dulce ponds located in Doñana National Park in southwestern Spain during different stages from 2016 to 2018. The results of this study have improved the understanding of the thermal structure and the surface–subsurface heat exchange in the ponds and highlighted the importance of groundwater discharge in the pond water balance. It also showed the heterogeneous nature of groundwater discharge through the bottom sediments of the Santa Olalla pond. These results are consistent with previous studies and strengthen the existing hydrological and limnological knowledge of these ponds located in the protected area which is receiving a great deal of public attention.

Keywords: *heat flow; surface water-groundwater interaction; hydrological monitoring; Doñana National Park*

III.1.1. Introduction

Doñana, in southwestern Spain, is an iconic World Heritage site within the Mediterranean region. The conservation of this ecosystem is particularly challenging, requiring coordinated actions across complex and sometimes very large watersheds. Although protected, Doñana is still affected by a range of threats. For example, water extraction and pollution have caused the degradation of a number of ponds within the wetland complex in spite of their protected status (Green *et al.* 2017). The Doñana area is located on the Atlantic Ocean coast, adjacent to the Guadalquivir River mouth (Figure 1a), and covers more than 3,000 km². Inside the limits of the 543-km² Doñana National Park is the Doñana

Biological Reserve (68 km²), where numerous ponds form during rainy periods and interact with local groundwater flow systems. Different regional and/or local flow systems occur at different times of the year depending on the presence of surface ponds and the water table position relative to the ponds (Lozano-Tomás, 2004).

Santa Olalla is the largest pond (25 ha) in the area and the only pond that is permanently flooded. Its maximum depth is 2.2 m, and overflows and merges with Dulce pond, on its western shore (see Figure 1), and with a series of small ponds existing on its eastern shore in unusually wet years. The surface watershed has a size of 155 ha, and its lowest point is near the center of the pond at an altitude of 2.5 m above sea level. Only

after intense drought periods has the pond been almost completely dry, so it is classified as a permanent water body. In such occasions, a number of submerged springs have been seen on its southern edge.

Santa Olalla is a groundwater flow-through pond located above an unconfined aquifer consisting of fine aeolian sands (Lozano-Tomas, 2004; Sacks *et al.* 1992). The regional groundwater flow direction in the Doñana aquifer is from northeast to southwest towards the Atlantic Ocean. Local groundwater discharge from the aquifer to the lowest parts of the sand dunes is the main water input to Santa Olalla and other ponds. Since the early 1970s, the area has been subjected to different pressures, especially due to water demands from crop irrigation and from a coastal resort which is located only 3.8 km from Santa Olalla pond and less than 1 km from other dried-out ponds such as Charco del Toro (Figure 1b). In this type of ecosystem, groundwater discharge/recharge

The theoretical base of using heat as a groundwater tracer was published in the 1960s, but recent work has significantly expanded the application to a variety of hydrogeological settings (Swanson and Cardenas, 2011; Bastola and Peterson, 2016; Irvine *et al.* 2015; McCallum *et al.* 2012). Temperature patterns started to be exploited to study subsurface flow systems. Early studies had several limitations, such as data-acquisition and computational techniques, although such limitations have been overcome throughout the years (Stonestrom and Constantz, 2003). Heat transport by groundwater has proven to be useful as a tracer to identify surface water infiltration, flow through fractures and flow patterns in groundwater basins. Temperature measurements can be analyzed for recharge and discharge rates or to estimate interchange with surface water, hydraulic conductivity of streambed sediments, and even basin-scale permeability.

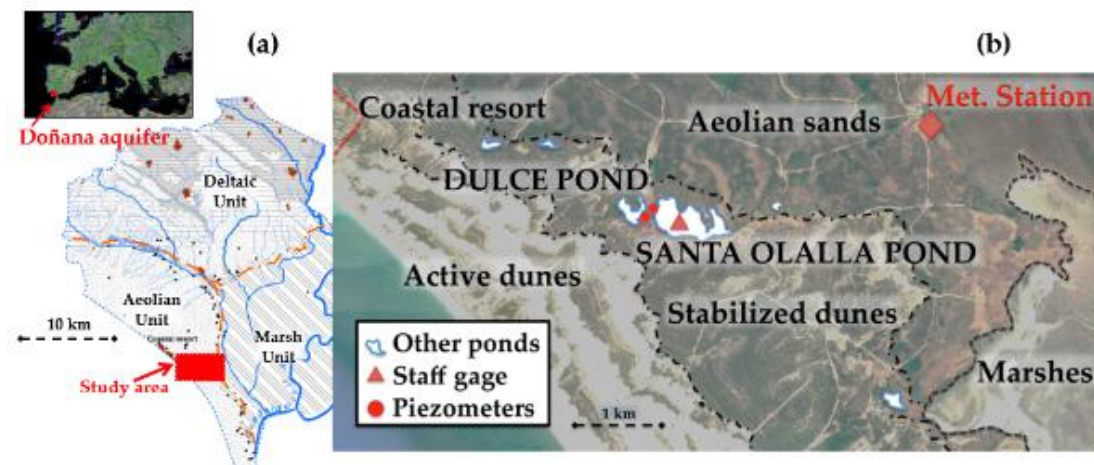


Figure 1. Study site: (a) Doñana aquifer in southwestern Spain showing main geological units, rivers and streams, as well as the study area; (b) Study area; meteorological station, staff gage in Santa Olalla pond. Dulce pond and other relevant ponds are highlighted, as well as the coastal resort. Active and stabilized dunes, aeolian sands and marshes are also marked.

is the most difficult component of the water balance to quantify. Therefore, in hydrogeological studies of ponds in particular and, in any hydrogeological research in general, different methodologies are used to estimate the groundwater component and compare the values to improve the confidence in estimated fluxes.

In Santa Olalla, groundwater inputs have recently been estimated via water balances and the segmented Darcy method (Rodríguez-Rodríguez *et al.* 2018), while aquifer permeability and transmissivity were recently estimated using the methods based on the tidal influence on the short-term fluctuations of the piezometric level near the

pond (Fernández Ayuso and Rodríguez-Rodríguez, 2018).

The objective of this study is to estimate the groundwater discharge from the sand aquifer to Santa Olalla pond in three different periods using different thermal approaches including field measurements, heat transfer modeling, and the analysis of thermal profiles. The results were compared to similar studies that were previously conducted in the pond.

III.1.2. Materials and Methods

Temperature was measured at three different periods: an intensive field campaign in July 2016 (1 in Figure 2), and two periods of hourly temperature data acquisition during a high water stage in spring 2017 (2 in Figure 2), and a low water stage from October 2017 to March 2018 (3 in Figure 2).

Surface and groundwater temperature and electrical conductivity (EC) were measured

with a portable multi-meter (HACH-HQ40D) calibrated before each field trip and using a PVC mini-piezometer to insert the probe, in July 2016. The mini-piezometer was driven approximately 0.5 m deep into the pond sediments by hand at 12 points within 5–10 m of the shore (Figure 3). In addition, several profiles and transects of water EC, temperature, and pH were done on the northwestern shore of the ponds (see Appendix A and Appendix B). As for the second and third stages of our study, a set of four auto logging temperature sensors (Maxim, iButtons DS1922L-F5) was installed inside a PVC tube attached to the Staff Gage of Santa Olalla pond. This tube was similarly driven 0.5 m deep into the pond sediments in the center of the pond. The deepest sensor was installed at a distance of 35 cm depth below the bottom of the pond. The iButtons were programmed to record temperature data at an hourly rate with a resolution of 0.0625 °C. Software 1D-Temp-Pro (Koch *et al.* 2015) was used for the analysis of one-dimensional vertical temperature profiles. This method numerically solves the flow and heat-transport

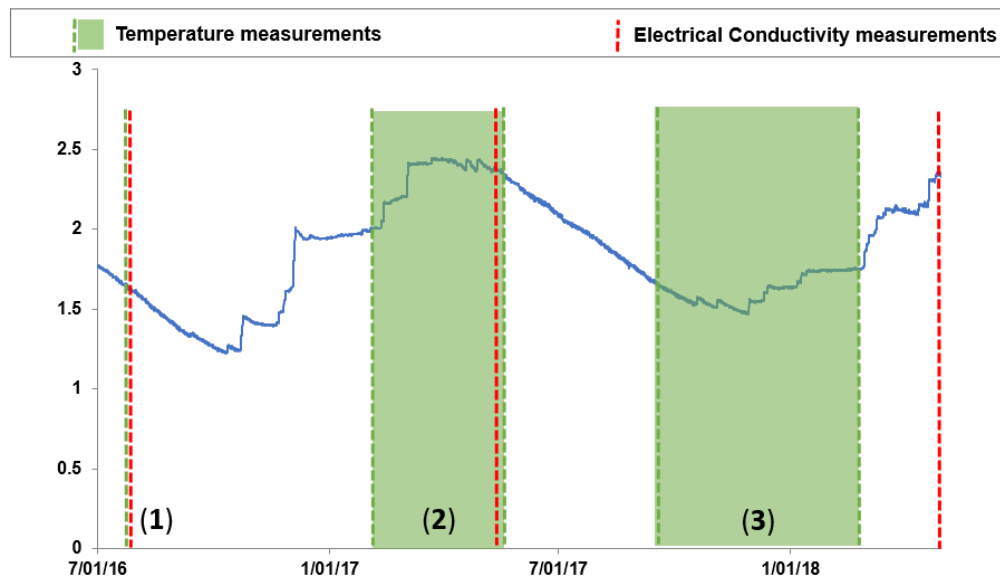


Figure 2. Water level in Santa Olalla pond from July 2016 to May 2018. (1) Measurement of surface and groundwater temperature (green) and electrical conductivity (red) in a two-day campaign along the pond's shoreline in July 2016. (2) Period for air, surface and groundwater temperature data acquisition at the staff gage (see Figure 3 for location) (high water stage). (3) Period for air, surface, and groundwater temperature data acquisition at the staff gage (low water depth). On 9 May 2018, after a rainy period, a surface water temperature, electrical conductivity (EC), and pH profile measured on the northwestern shore of the pond.



Figure 3. The locations of the measurement points along the pond’s shoreline using a portable mini-piezometer (12th–13th July 2016); the piezometer (17 m depth), the surface water temperature—EC profile and the pond-shore temperature—EC transect (9th May 2017 and 9th May 2018). In the center of the figure, the staff gauge with the iButtons (red circles) used for the heat transfer modeling is shown (distance from the pond’s floor is expressed in cm). Aerial Photo was taken on 26 July 2017 (Source: Google Earth).

equations and uses a graphical software package for simulating energy transport in variably saturated porous media (VS2DI). The program allows users to calibrate VS2DH models against measured data to estimate vertical groundwater/surface-water exchange.

Temperature variations throughout the year at several depths have proven to be adequate to reproduce such water exchange with this transient state model. Parameters used in the modeling are shown in Table 1.

Table 1. Parameters used in the thermal modeling (1D-Temp-Pro)

Modeling Conditions 1d Temp Pro V.2	
Porosity	0.3 (m ³ /m ³) ¹
Thermal Conductivity	1 (W/m°C) ²
Sediment Heat Capacity	3.3 × 10 ⁶ (J/m ³ °C) ²
Dispersivity	5 × 10 ⁻⁴ m ³

III.1.3. Results

III.1.3.1. Field Campaigns in May–July (2016–2017–2018)

Figure 4 shows the water temperature and EC measured during the summer field

campaign on 12th and 13th July 2016. Surface water EC was nearly constant in the perimeter of the pond with values ranging from 10.47 to 10.70 mS/cm at 25 °C. Surface water EC measured at sampling point 7 (13.3 mS/cm) is not representative for the pond and can be considered as an outlier, as this section of the

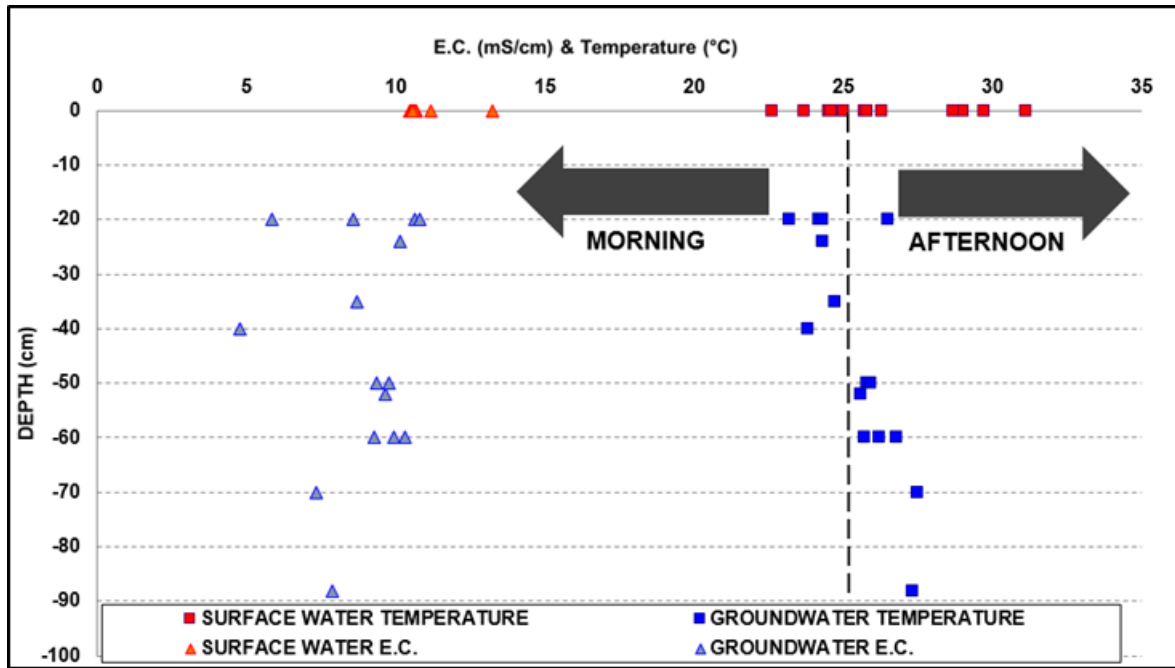


Figure 4. Water EC (left) and temperature (right) vs. depth on 12–13 July 2016. Vertical dotted line distinguished between morning and afternoon water temperature measurements.

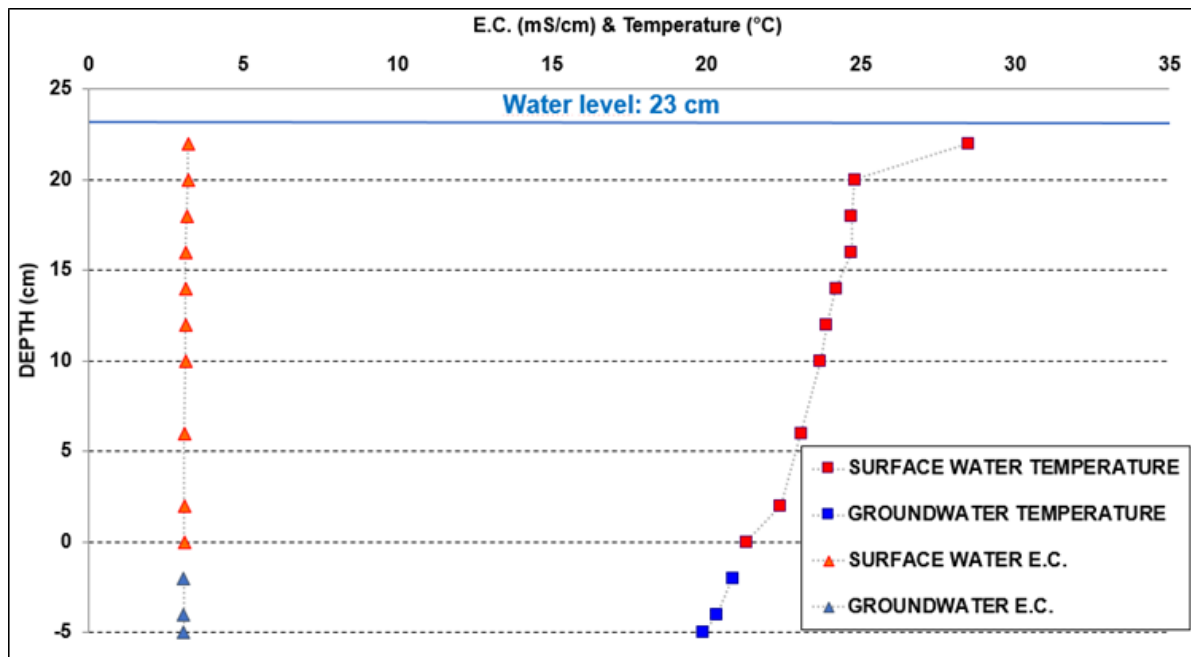


Figure 5. EC and water temperature vs. depth on the northwestern shore of the pond during the field campaign of May 2017.

pond was separated from the main water body, forming a small pool on the measurement date (13th July). Consequently, the water at point 7 experienced a greater evaporative concentration. Groundwater EC was lower than surface water EC in all the cases, ranging from 4.77 mS/cm to 10.7 mS/cm. Lower groundwater EC values were detected on the

southwestern shore. No significant correlation between water EC and depth were observed (Figure 4).

Surface and groundwater temperatures varied a great deal. The maximum differences between surface water and groundwater temperatures were mostly observed in the

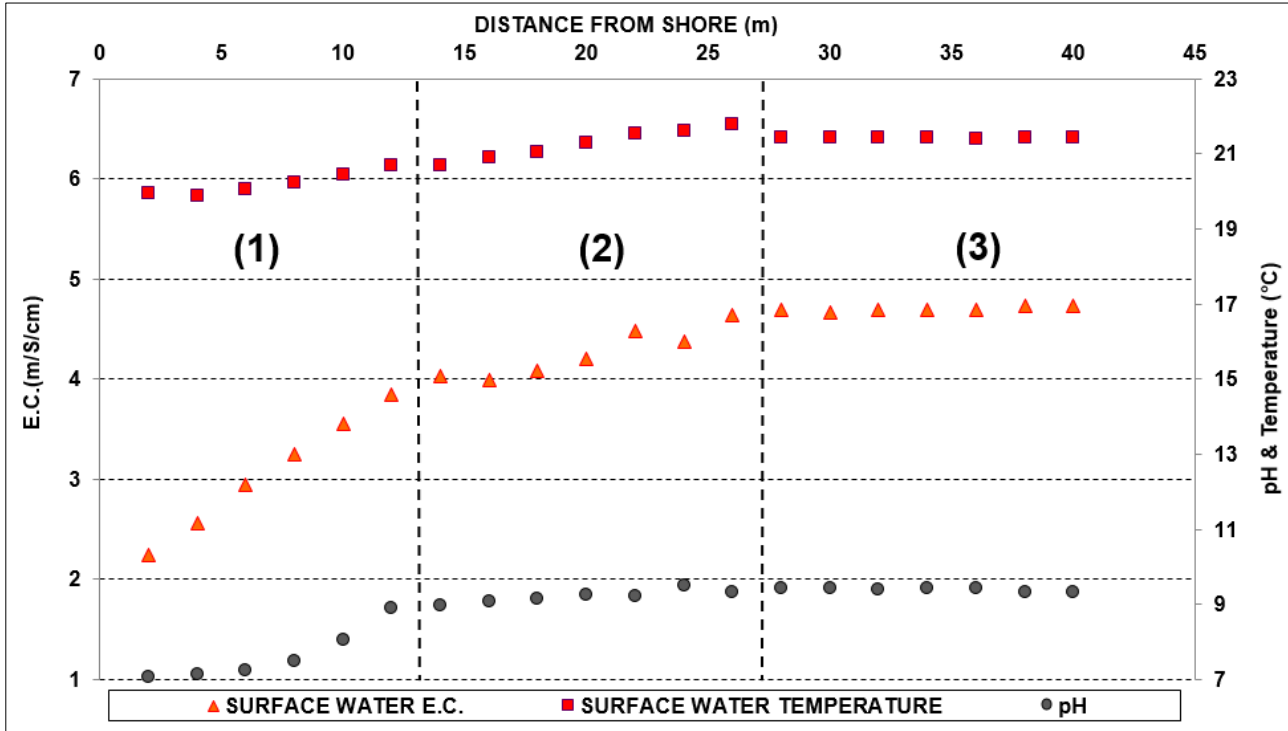


Figure 6. Water EC vs. distance from shore (left) and pH and water temperature vs. distance from shore (right) during the field campaign of 9 May 2018.

afternoon, whereby groundwater was approximately 3 °C cooler than surface water. In the morning hours of the next sampling date, the reverse process occurs. Surface water was slightly cooler than groundwater, this behavior being smoother until midday. After midday, similar temperatures were measured in ground and surface water. As a rule of thumb, surface water temperatures were much more variable and greater than groundwater temperatures.

On May 2017 and 2018, EC and temperature profiles were measured on the northwestern shore of Santa Olalla pond (Figure 5 and Figure 6). On 9th May 2017, a profile from the water surface down to 5 cm into the bottom sediment was made (Figure 5). No significant variation was found in EC which ranged from 3.22 to 3.08 mS/cm. Nevertheless, the water column on the pond was thermally stratified, from nearly 29 °C near the surface to less than 20 °C below the bottom. Much of the variation occurred between the surface and the 5 cm below the surface indicating the surface heating by solar radiation. Groundwater temperature measured in the on-shore piezometer (Figure 7) was 22.6 °C and the EC was much lower (216 μ S/cm)

than pond water. The piezometric level was 53 cm above the ground, indicating the upward and pond-ward hydraulic gradient, meaning that groundwater discharged from the aquifer to the pond (Figure 8).

On 9th May 2018, after an intense rainfall period on the Atlantic coast of Spain and the Ebro Basin that lasted from March to the end of April, water EC, pH, and temperature were measured along the same transect as in May 2017 (Figure 6). On this occasion, surface measurements were made from the shore to the center of the pond every two meters. Measurements ended when the values of every parameter were found to be stable, this was at a distance of about 40 m from the shore (Figure 6). The EC, increased from 2.24 to 4.70 mS/cm, while the groundwater EC in the piezometer was much lower at 0.234 mS/cm, very similar to the EC measured in the previous year. Groundwater temperature was 19.8 °C and pH was 7.10 (Figure 8). The shore-to-center change in the measured variables in this period (Figure 6) suggests that the groundwater input is a major component of the water balance in the pond, as sketched in Figure 8. On the other

hand, it seems clear that three zones (depicted in Figure 6 as 1, 2 and 3) can be distinguished: 0–12 m, 12–26 m and 26–40 m. In the 0–12 m zone, all the measured properties are increasing, in the 12–26 m zone, temperature and EC are increasing, and in the 26–40 m zone all are uniform. There is even a clear difference in the slope of EC in each of the three zones as can be seen in Figure 6.

A similar transect measurement was made the same day in Dulce pond, where a piezometer similar to the one at Santa Olalla (Figure 7) was installed (see Figure 1b for location). No significant variation was found in the water EC in Dulce pond, although a hydraulic head at a depth of 15 m in the on-shore piezometer was 70 cm above the ground surface indicating the pond-ward flow of groundwater. The water EC was nearly constant, ranging from 1.1 to 1.2

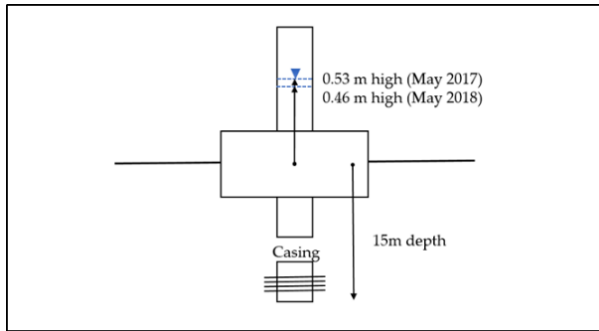


Figure 7. Sketch of the piezometer located near the northwestern shore of Santa Olalla pond. Groundwater level measured during the field campaign of May 2017 and May 2018. Dulce pond's piezometer has similar characteristics.

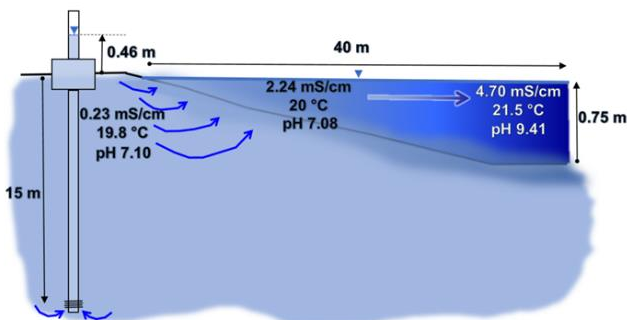


Figure 8. Sketch of the hydrological flows taking place at the northwestern shore of Santa Olalla pond in May 2018.

mS/cm along the transect. On the other hand, pH ranged from 7.1 to 8.6 at a distance of 20 m from the shore. Temperature ranged from 20.0 to 21.8 °C in the same transect (see Appendix B for details). Groundwater in the piezometer had a temperature/EC/pH of 20.0 °C, 0.187 μ S/cm, and 8.25, respectively.

III.1.3.2. Heat Transfer Modelling to Estimate Groundwater Discharge

Table 1 lists the parameters used in the thermal modeling. Boundary conditions (position of the temperature sensors) are shown in Figure 3. Thermal conductivity is a property related to the hydraulic conductivity (k) in heat-flow modeling, although k varies over a much broader range than the former. Parameters used in the thermal modeling (see Table 1) were based on bibliography References (Goto and Matsubayashi, 2008; Silliman and Booth, 1993; Jensen *et al.* 1993; Rosenberry and Hayashi, 2013). The modeling carried out with 1D temp pro V2 showed different results for each study period. Input parameters used for both periods were the same. Porosity was 0.3, thermal conductivity 1 W/m°C, sediment heat capacity 3.3×10^6 J(m³/°C) and dispersivity 0.0005 m (Silliman and Booth, 1993; Jensen *et al.* 1993). These inputs were chosen according to the values proposed by the authors Rodríguez-Rodríguez *et al.* (2018) and Fernández Ayuso and Rodríguez-Rodríguez (2018) for the porosity, Goto and Matsubayashi (2008) for the thermal conductivity and the sediment heat capacity, and Jensen *et al.* (1993) for the dispersivity. The model fitting was found to be very accurate to the measured values. The obtained discharge for the first study period (14 February 2017–16 May 2017) resulted on 0.36 hm³/year. This value corresponds to a groundwater discharge through the perimeter of the pond, considering an average depth of 1.5 m. The hourly data series of the surface water, surface–groundwater interface, and groundwater

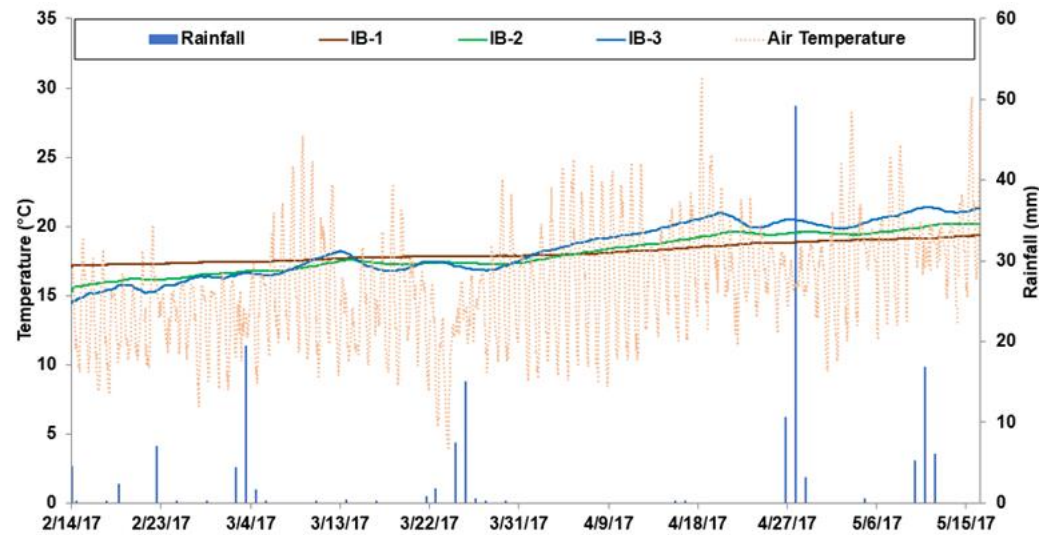


Figure 9. Hourly evolution of the surface, interface, and groundwater temperature in the center of Santa Olalla pond, from February to May 2017. **IB-3** corresponds to the iButton placed at a distance of 0.25 m from the pond's floor. **IB-2** corresponds to the iButton placed directly on the pond's floor, and **IB-1** corresponds to the sensor placed at a depth of -0.35 m below the pond's floor. Air temperature is also plotted, although air temperature was not used in the model setup. In the same sense, rainfall events are also shown.

temperature in the center of Santa Olalla pond, from February to May 2017 are shown in Figure 9. The water temperature recorded by the deepest sensor, IB-1, was fairly constant, increasing smoothly and at a constant rate from 17 to 18.5 °C during the study period. The temperatures in the pond's bed (IB-2) and above (IB-3) were not influenced by diurnal changes in air temperature, although such changes could be high, more than 15 °C between midday and night (Figure 9). It should be noted that IB-2 and IB-3 had a column of water of deeper than 2 m above them (Figure 2), buffering the changes in the water surface temperature.

On the other hand, longer-term declines of air temperature, as well as rainfall events, produces a temporal cooling of the surface waters of the pond that, due to mixing and processes of advection, reach the bottom of the pond, lowering the temperature of IB-2 and IB-3, but not IB-1. This is indicative of a process of groundwater discharge from the aquifer to the pond, as sensor IB-1, located beneath the sediment, is influenced by cooler groundwater temperature (Silliman *et al.* 1993). Otherwise, thermal changes in the

surface water would affect the groundwater temperature.

III.1.3.3. Thermal behavior and heat transfer modelling to estimate groundwater during low water depth

Groundwater discharge values during the second period (1 December 2017–10 February 2018) obtained from the heat transfer modeling were of an order of magnitude lower, that is, 0.05 hm³/year. Figure 10 shows the temperature in such a period of low water stage in Santa Olalla pond. The vertical positions of IB-1, IB-2, and IB-3 were the same as Figure 9 except that the water stage was much lower (see Figure 2).

From September 2017 to February 2018, the magnitude of temperature oscillations in IB-3 (Figure 10a) was higher than that during the period of higher water stage in February–March 2017 (Figure 9), indicating that the temperature oscillations

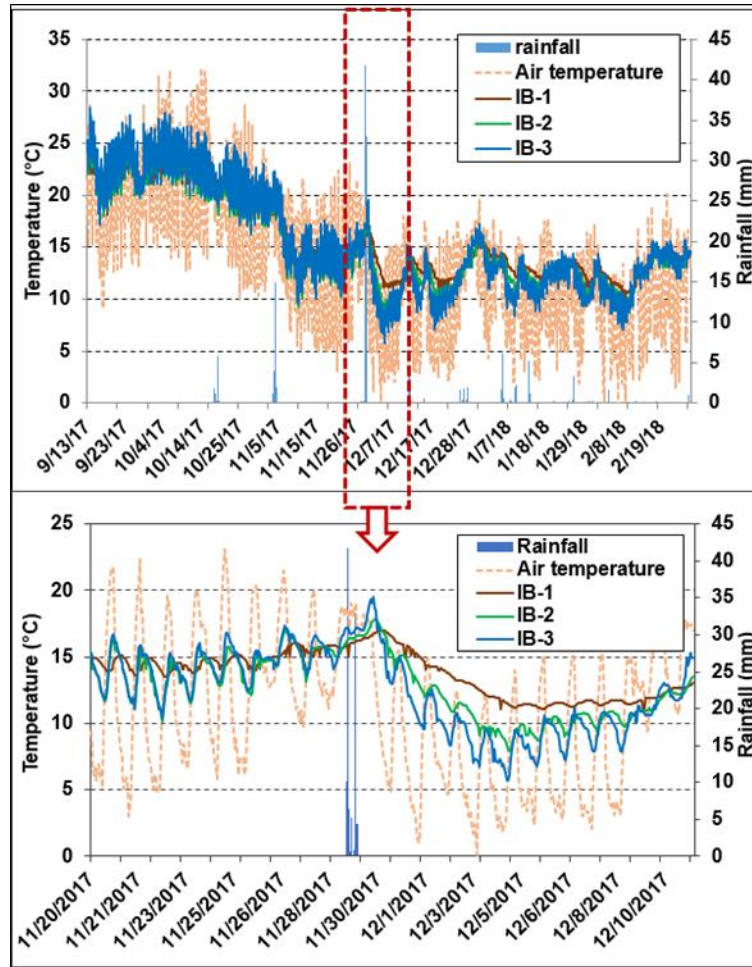


Figure 10. Hourly evolution of the surface, interface, and groundwater temperature in the center of Santa Olalla pond, from September 2017 to February 2018. Rainfall events are also shown.

from the water surface reached the bottom of the pond. In November 2017, pond water temperature (IB-3) oscillated between 12 and 16 °C following a diurnal pattern (Figure 10b). Groundwater temperature (IB-1) also oscillated daily, between 14 and 15 °C indicating the effects of heat conduction through the bottom sediment. This process of groundwater recharge during low water depth periods was taking place until a rainfall event. Such event totalized c. 80 mm of precipitation over the pond as well as an increment of c. 50 cm in the pond's water level, and took place from 29 to 30th November 2017. As it can be seen in Figure 10, surface water was lowered from 15 to 5 °C, oscillating in a daily pattern, whereas groundwater remains stabilized daily, but water temperature cooled from 16 to 12 °C during a five-day time interval (from 30

November 2017 to 4 December 2017), suggesting groundwater recharge from the center of the pond to the aquifer throughout all the third stage of this study.

III.1.4. Discussion

This study has shown that the groundwater inputs to Santa Olalla pond had high seasonal variability. In addition, the perimeter of the pond seems to be the preferential area of groundwater discharge (inflow) as stated by other authors (Sacks *et al.* 1992). The center of the pond, where the staff gage was placed, seems also to be a discharge (inflow) area especially during high water level stages, where hydraulic gradients are higher. Other authors did similar experiments in Dulce and Santa Olalla ponds in July and December 1985

(Sacks *et al.* 1992). They also applied a 2D model to quantify flows from and to the pond, as well as the transport of solutes. The results obtained by these authors indicate that Santa Olalla acts like a discharge pond during the wet phase of a hydrological cycle (December 1985), but they point to an inversion of the hydraulic gradient during the dry phase (July 1985), in which a water recharge toward the aquifer takes place, bringing salts via advection methods. The average EC in the groundwater oscillated between 0.2 mS/cm in deep (15-m) piezometers and 1.5 mS/cm in shallower (3.5-m) piezometers.

In a more recent work made in 2017 (Rodríguez-Rodríguez *et al.* 2018) the groundwater discharge rate estimated using a water balance method was 0.40 hm³/year to Santa Olalla pond. Higher values for groundwater discharge (c. 1.30 hm³/year) were obtained by the segmented Darcy method, also applied to the pond (Rodríguez-Rodríguez *et al.* 2018). In this case, some of the discharge could not eventually go to the pond, but to the coast or to the Vera ecotone since the volumes of flow are higher than those estimated for the same period of time using the water balance method.

III.1.5. Conclusions

In this study, temperature, EC, and pH of pond water and groundwater were used as tracers to detect groundwater—surface water interactions and the hydrological functioning in a permanent pond, Santa Olalla, located above highly permeable dune sands. A semi-permanent Dulce pond adjacent to Santa Olalla was also investigated. The results showed a complex hydrological pattern likely reflecting the existence of several groundwater flow paths, ranging from local to regional, that affect the ponds in different periods and different water stages.

First, the field data collected at several periods during 2016–2018 suggest a net groundwater discharge throughout the

shores, which contributes greatly to the water balance of the pond. Water EC measurements on the western shore after a two-month period of high rainfall revealed a remarkable gradient of more than +6 mS/100 m on a 40 m transect, indicating a local groundwater flow path discharging fresh groundwater onto the pond. At the same time, a similar transect made in nearby Dulce pond, did not show any change in water EC (gradient of 0 mS/100 m). On the other hand, a pH gradient was detected in both ponds, suggesting that this water characteristic is much more influenced by biological processes, such as the photosynthetic activity, taking up CO₂ dissolved in the water and, therefore, raising the pH from the shore to the center of the pond.

Secondly, temperature profiles made in the center of Santa Olalla pond during high and low water level periods suggests a net groundwater discharge during high water levels, but seepage of surface water to the aquifer (recharge) during low water stages. This leakage of pond's water to the aquifer could also explain why the water of Santa Olalla pond ranges from brackish in winter to saline in summer: Some of the salts have a way out of the system via recharge to the aquifer. Otherwise, the water salinity would have been much higher, of a brine type. In the same sense, and in an inter-annual behavior, during dry years, solutes in Santa Olalla may go from the pond to the aquifer, and during wet years this process is interrupted because the groundwater levels are above surface levels all around the shore. Of course, there could be other ways to lose salts from the pond (e.g., via Aeolian processes, when the wet surface of the pond shrinks in summer). Only during exceptionally rainy years, Santa Olalla and Dulce ponds connect with each other and form a continuous water body. Saline water from Santa Olalla then mixes with Dulce fresh water, and a brackish-water pond is created. This is another way out for Santa Olalla solutes.

Author Contributions

M.R.-R. and A.F.-A. conceived, designed and performed the experiments; A.F.-A. analyzed and executed the thermal model; F.M.-M. contributed to the analysis and conceptualization of the results; M.R.-R. and M.H. wrote the paper.

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Conflicts of Interest

The authors declare no conflict of interest.

III.2: Assessment and hydrochemical modeling of the sand dune ponds located in the Doñana Biological Reserve (Huelva, Spain).

Caracterización y modelización hidroquímica de las lagunas peridunares situadas en la Reserva Biológica de Doñana (Huelva, España).

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RESUMEN

Se ha realizado la caracterización hidroquímica de las aguas superficiales y subterráneas en 7 lagunas peridunares del Parque Nacional de Doñana y 7 piezómetros situados en sus orillas, entre el año 2016 y el año 2018. En total se han analizado 80 muestras de aguas superficiales y 70 de aguas subterráneas, Los rangos de salinidad y pH registrados en las aguas superficiales oscilaron entre 0,37 y 28,6 mS/cm y 7,16 y 9,68, respectivamente, mientras que para las aguas subterráneas, estas variables oscilaron entre 0,17 y 0,70 mS/cm y 6,24 y 7,59. El análisis de iones mayoritarios refleja facies desde mixtas-sódicas a cloruradas-sódicas para las aguas superficiales y desde mixtas a cloruradas-sódicas para las aguas subterráneas. Por otro lado, en el sistema Dulce-Santa Olalla-Pajas, se han realizado análisis isotópicos de D y O¹⁸ y la modelización hidroquímica de iones mayoritarios con Phreeqc antes del estiaje y en periodo invernal. Tanto el análisis hidroquímico como el isotópico revelan una marcada diferencia entre las aguas superficiales y subterráneas, así como una marcada variabilidad estacional. En el caso de las aguas superficiales, las diferencias hidroquímicas encontradas en las lagunas están relacionadas con su diferente funcionamiento hidrológico. En las aguas subterráneas, dicha variabilidad viene condicionada por la profundidad del piezómetro en el que se ha tomado cada muestra.

Palabras clave: *análisis de iones mayoritarios, ecosistemas acuáticos, modelización hidroquímica, isótopos estables.*

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III.2.1. Introducción

El Parque Nacional de Doñana está considerado como uno de los humedales más importantes de Europa, debido a que constituye un reservorio de biodiversidad y alberga ecosistemas únicos. Tanto los cambios globales como las presiones locales están afectando al mantenimiento de dichos ecosistemas, de tal manera que son numerosas las publicaciones que ponen de manifiesto que los límites de resiliencia en

algunos de ellos están siendo sobrepasados (Green *et al.* 2017). Uno de estos ecosistemas lo constituyen las lagunas situadas sobre las dunas estabilizadas de los mantos eólicos de Doñana (Figura 1). El seguimiento de los niveles de aguas superficiales y subterráneas en las principales lagunas y su entorno se está llevando a cabo en la actualidad por la Confederación Hidrográfica del Guadalquivir, gracias a diversos convenios con entidades públicas de investigación como el IGME o la Universidad Pablo de

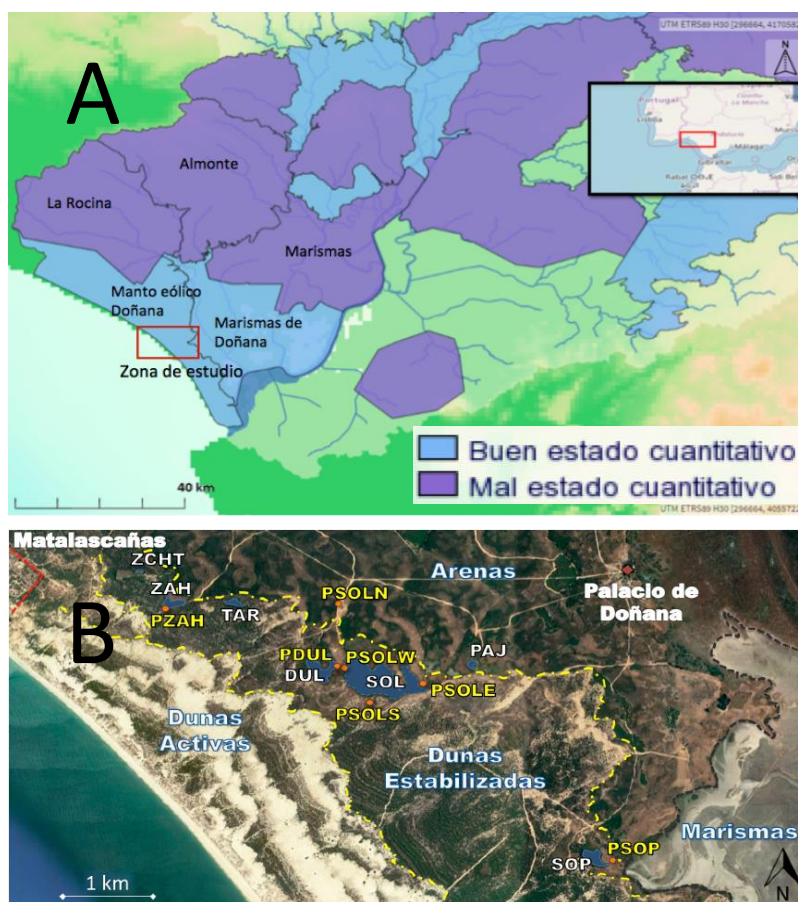


Figura 1. Área de estudio. A) Localización de las MASub. del Parque Nacional de Doñana y su estado cuantitativo (Fuente: www.chguadalquivir.com, fecha de la consulta: Mayo 2018). B) Localización de las lagunas y los piezómetros estudiados (puntos naranjas). Se aprecia en el sector noroeste la población de Matalascañas y en el noreste el Palacio de Doñana. ZCHT: Zacallón* de la laguna del Charco del Toro; ZAH: Laguna de Zahillo; TAR: Laguna del Taraje; DUL: Laguna Dulce; SOL: Laguna de Santa Olalla; PAJ: Laguna de Las Pajas; SOP: Laguna de Sopotón; PZAH: Piezómetro Zahillo; PDUL: Piezómetro Dulce; PSOLN: Piezómetro Santa Olalla Norte; PSOLS: Piezómetro Santa Olalla Sur; PSOLE: Piezómetro Santa Olalla Este; PSOLW: Piezómetro Santa Olalla Oeste; PSOP: Piezómetro Sopotón. *Excavación del terreno que llega al nivel freático, frecuente en Doñana, y que se usaba tradicionalmente como abrevadero para el ganado. Se ha seleccionado este punto para la toma de muestras de agua por encontrarse seca la laguna del Charco del Toro desde 2010.

libre de las arenas eólicas, sistema que ha sido recientemente definido como Masa de Agua Subterránea Manto eólico Doñana y al que se otorga la categoría general de Buen estado cuantitativo (Figura 1-A). Es el objetivo de este trabajo estudiar, mediante el análisis de información hidroquímica, el estado cualitativo de las aguas de estas lagunas, así como de las aguas subterráneas en su entorno y contrastar los resultados obtenidos en los recientes estudios sobre aspectos cuantitativos (Rodríguez-Rodríguez *et al.* 2017).

II.2.2. Metodología

Las características físico-químicas del agua tomadas en campo (temperatura del agua, pH y CE) se realizaron con una sonda multiparamétrica portátil (HACH HQ 40D®), ver Figura 2. El análisis de componentes mayoritarios de las 150 muestras de agua tomadas en las 7 lagunas estudiadas y en los 7 piezómetros cercanos a sus orillas se ha realizado mediante cromatografía iónica (equipo ICS-1000, DIONEX®). El análisis de bicarbonatos se

realizó mediante valoración colorimétrica, Las muestras de agua superficial se tomaron a varios metros de la orilla de las lagunas y las de aguas subterránea mediante un toma-muestras integral a una profundidad de, aproximadamente, un metro bajo el nivel piezométrico.



Figura 2. Medida de parámetros físico-químicos *in situ* en aguas superficiales de la laguna de Zahillo (30/04/2018). En la imagen se puede observar la regleta de nivel en la que se encuentra instalado un registrador en continuo de la profundidad de la lámina de agua, temperatura y C.E. del

Para el almacenamiento se emplearon en todos los casos botes de plástico de 0,5 litros de capacidad y se trasladaron en frío al laboratorio de Hidroquímica de la Universidad Pablo de Olavide, donde se analizaron en los días siguientes. Los análisis isotópicos del agua se realizaron en los laboratorios del Centro de Hidrogeología de la Universidad de Málaga. El análisis de los resultados obtenidos se ha ejecutado utilizando los programas AquaChem© para el establecimiento de la base de datos hidroquímica y el paquete R vegan (Oksanen *et al.* 2018) para el análisis estadístico de los resultados, La modelización hidroquímica se realizó mediante el software PHREEQC, versión 3 (Parkhurst y Appelo, 2013).

III.2.3. Resultados

En la Figura 3 se pueden apreciar las características hidroquímicas del agua de las lagunas estudiadas, así como del Zacallón del

Charco del Toro (ZCHT). En general, predominan las facies cloruradas sódicas en la mayoría de las lagunas. En el caso del sistema Dulce-Santa Olalla-Pajas (DUL-SOL-PAJ) se ha optado por la representación en un único diagrama, ya que se trata de tres lagunas que en periodos lluviosos se llegan a unir, mezclándose sus aguas durante un periodo de tiempo. En cualquier caso, esto no sucede todos los años y se aprecia una tipología hidroquímica diferente para cada laguna. La laguna de Santa Olalla es la que presenta aguas más saladas y facies clorurado sódicas incluso en invierno, llegando a superar concentraciones de más de 100 meq/L tanto de Cl como de Na. La laguna Dulce presenta aguas clorurado sódicas o clorurado mixtas, aunque las concentraciones máximas de Cl y Na no superan generalmente los 10 meq/l. La laguna de las Pajas presenta aguas de menor contenido salino y facies clorurado mixtas o mixtas. Las otras tres lagunas (ZAH, SOP y TAR) presentan aguas, en general, cloruradas sódicas o mixtas. La laguna de Zahillo es la que presenta aguas menos mineralizadas, facies mixtas y mayores variaciones estacionales de la concentración iónica. Finalmente, las aguas del ZCHT contienen algo más de sulfato y magnesio que las aguas superficiales.

En la Tabla 1 se pueden observar los valores medios y medianos de las principales características hidroquímicas del agua en las lagunas seleccionadas y el ZCHT. En general el valor mediano (i.e. percentil 50) de salinidad del agua suele ser menor que el valor medio, ya que es los sistemas lagunares temporales suelen registrarse picos de salinidad y C.E. del agua que aumentan del valor de la media. Por tanto, el valor de la mediana se considera más representativo para hacer referencia a la salinidad más común o más frecuente en cada sistema. En las lagunas estudiadas, Zahillo es la que presenta un menor valor de esta variable (salinidad mediana: 605,56 mg/L). De hecho, es cinco veces menor que la laguna más salina, Santa Olalla (3333,80 mg/L).

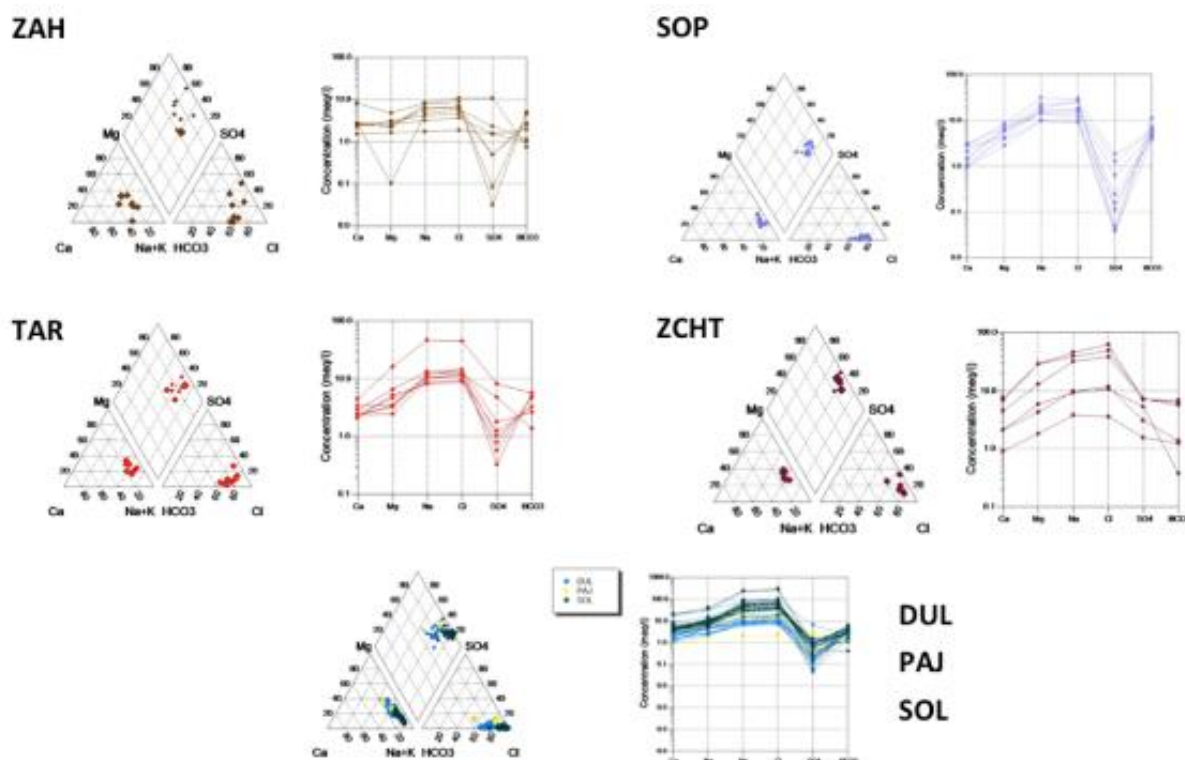


Figura 3. Diagramas de Piper y Shöeller-Berkaloff en las muestras de agua de las lagunas estudiadas y en el zacallón del Charco del Toro. El sistema Dulce-Santa Olalla-Pajas se ha representado de manera conjunta. Estas tres lagunas llegan a unirse en años muy lluviosos

Esta relación entre las salinidades de ZAH y SOL (1:5) aumenta hasta una relación 1:8 si comparamos las concentraciones de cloruros en lugar de la salinidad total (216 mg/L de Cl frente a 1799 mg/L de Cl, ver Tabla 1). SOP es la más salina tras SOL en una relación SOP:SOL de 1:2 (SOP: 1405,15 mg/L), seguida de las lagunas PAJ, TAR y DUL (1184,27 mg/L, 1080,50 mg/L y 904 mg/L de salinidad mediana, respectivamente). El ZCHT tiene una salinidad mediana de 2035,87 mg/L, si bien es la que presenta una mayor concentración de SO₄ (296,71 mg/L). Cabe señalar que las concentraciones de minoritarios (NO₃ y PO₄) son muy bajas o indetectables en las lagunas y en ZCHT. Los valores de pH son ligeramente básicos, entre 7,4 y 8,8 salvo en la laguna de Zahíllo que son inferiores.

En la Figura 4 se pueden apreciar las características hidroquímicas del agua en los piezómetros PDUL, PSOL (N, S, E y W), PSOP y PZAH. Predominan las facies cloruradas sódicas o mixtas y la

mineralización de las aguas es más débil que en las aguas superficiales en la mayoría de los casos.

En la Tabla 2 se pueden observar los valores medios y medianos de las principales características hidroquímicas del agua en los piezómetros seleccionados. En este caso, las aguas más salinas se corresponden con el piezómetro instalado en la cubeta de la laguna de Zahíllo (1027,72 mg/L de salinidad mediana). Este hecho contrasta con las características del agua de la laguna, que es la menos mineralizada de las estudiadas. Esta circunstancia se discutirá en el apartado siguiente. En el resto de los piezómetros se aprecia una marcada diferencia entre las salinidades de los piezómetros más en torno a 120 – 160 mg/L y los piezómetros someros (2 - 3 m) como PSOLE, PSOLS o PSOP que presentan salinidades medianas en torno a los 500 – 700 mg/L. En cualquier caso, estas salinidades son profundas (15 - 17 m) como PDUL o PSOLW que presentan salinidades medianas inferiores a las salinidades del agua de sus lagunas respectivas, como se ha

III. Thermal and hydrochemical methods

Tabla 1. Valores medios y medianos de las principales características hidroquímicas del agua en las lagunas estudiadas. N: Número de análisis realizados. Sal.: Salinidad (mg/L); CE: Conductividad eléctrica ($\mu\text{S}/\text{cm}$); concentración de aniones y cationes expresada en mg/L.

PERIODO DE ESTUDIO		N	Sal	CE	pH	Cationes				Aniones						
						Na	K	Mg	Ca	CO ₃ Ca	F	Cl	NO ₃	PO ₄	SO ₄	
DUL	19	04/05/2016	Media	1489,71	2537,79	8,40	377,63	17,75	76,87	64,02	182,20	1,45	741,28	3,51	0,04	36,05
		-														
		09/05/2018	Mediana	904,41	1569,00	8,58	195,86	10,43	52,78	41,97	167,75	1,08	384,24	0,04	0,00	11,64
PAJ	3*	12/12/2016	Media	1125,43	1883,33		275,90	8,22	68,91	52,41	133,69	2,67	497,84	0,15	0,01	85,64
		-														
		26/01/2017	Mediana	1184,27	2160,00		314,17	10,09	82,64	59,73	88,45	2,44	513,66	0,14	0,00	106,48
SOL	24	04/05/2016	Media	4401,56	8169,56	8,78	1330,18	47,19	129,34	109,89	202,22	5,55	2517,81	0,90	0,11	33,36
		-														
		09/05/2018	Mediana	3333,80	6190,00	8,90	948,00	38,63	109,12	80,89	190,63	3,54	1799,89	0,03	0,00	34,58
SOP	9	04/05/2016	Media	1515,65	2329,89	7,82	384,98	17,89	67,79	35,93	354,14	2,22	624,43	0,77	0,01	22,68
		-														
		30/04/2018	Mediana	1405,15	2240,00	7,98	364,42	15,64	68,83	28,87	320,25	1,64	583,76	0,05	0,00	7,30
TAR	8	12/12/2016	Media	1373,07	2864,63	7,78	344,96	12,14	68,05	56,00	226,84	0,80	560,80	0,02	0,60	111,45
		-			7,72											
		30/04/2018	Mediana	1080,50	1950,00		249,04	10,65	48,67	48,68	198,25	0,61	430,81	0,00	0,76	54,63
ZAH	8	12/12/2016	Media	671,18	1525,75	7,16	119,30	7,18	29,72	62,34	148,88	1,32	217,02	0,38	0,03	102,81
		-														
		30/04/2018	Mediana	605,56	1077,50	7,32	122,42	6,15	30,68	51,72	134,20	1,12	216,70	0,05	0,00	47,45
ZCHT	6*	07/09/2016	Media	2306,74	3719,17	6,86	534,32	11,97	167,67	80,23	221,13	0,81	1037,23	1,83	0,00	252,71
		-														
		09/05/2018	Mediana	2035,87	3735,00	6,86	479,32	10,35	114,27	67,32	213,50	0,97	892,68	0,11	0,00	296,71

*El número de análisis en los casos de PAJ y ZCHT no es suficiente para establecer valores estadísticos representativos

comentado. Los valores de pH suelen ser cercanos a la neutralidad o incluso menores.

III. Thermal and hydrochemical methods

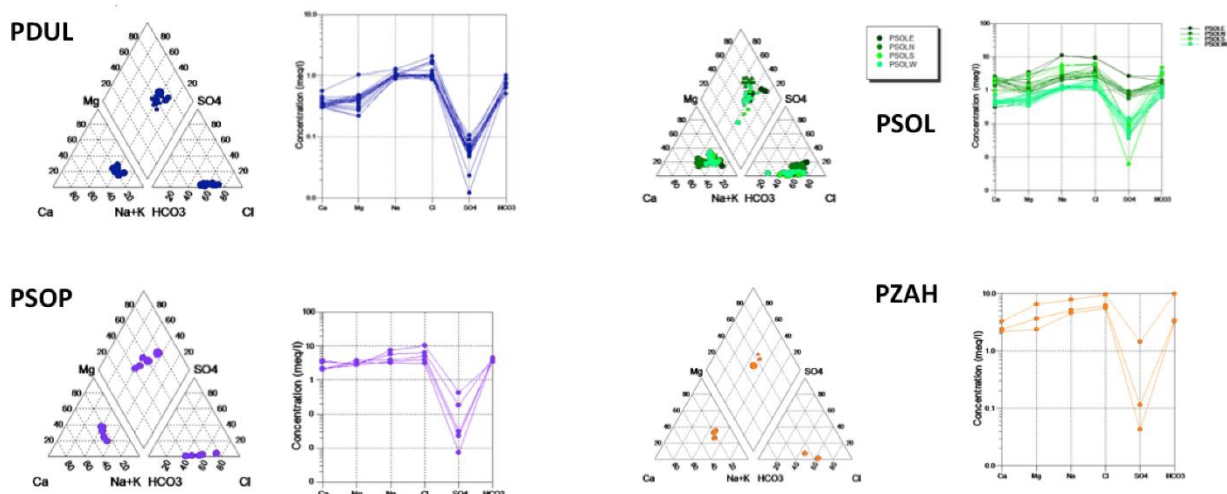


Figura 4. Diagramas de Piper y Shöeller-Berkaloff en las muestras de agua subterránea.

Tabla 2. Valores medios y medianos de las principales características hidroquímicas del agua en los piezómetros seleccionados. N: Número de análisis realizados. Sal.: Salinidad (mg/L); CE: Conductividad eléctrica (μS/cm); concentración de aniones y cationes expresada en mg/L.

N			PERIODO DE ESTUDIO	Sal	CE	pH	Cationes				Aniones					
PDUL	20	04/05/2016 - 09/05/2018	Media	137,51	216,58	7,1	24,40	8,56	5,38	7,44	46,74	0,09	39,13	2,56	0,12	2,97
			Mediana	121,19	187,75	7,07	23,74	1,85	4,88	6,80	45,75	0,01	35,81	1,81	0,01	2,64
PSOLE	4	07/09/2016 - 15/01/2018	Media	658,56	1344,50	7,12	164,00	9,60	27,10	26,04	131,18	0,13	228,01	7,22	0,05	64,58
			Mediana	766,74	1539,50	7,12	187,19	10,44	30,73	30,96	142,97	0,11	263,55	1,48	0,02	64,67
PSOLN	12	08/06/2016 - 30/04/2018	Media	361,89	645,42	7,17	56,42	6,59	12,93	39,31	95,44	0,09	114,24	0,75	0,07	35,69
			Mediana	359,40	595,00	7,20	56,12	1,50	11,89	41,09	91,50	0,01	110,31	0,17	0,01	35,46
PSOLS	4	07/09/2016 - 15/01/2018	Media	521,93	697,00	7,22	104,10	8,29	22,74	27,56	205,88	0,11	150,72	0,06	0,03	1,97
			Mediana	518,37	644,50	7,20	27,17	1,95	5,83	8,48	64,81	0,01	43,75	1,37	0,01	5,62
PSOLW	21	04/05/2016 - 09/05/2018	Media	162,95	356,19	6,69	26,77	7,26	6,55	8,85	64,20	0,17	50,66	1,41	0,02	4,29
			Mediana	162,21	266,00	6,70	26,75	2,34	6,38	8,79	61,00	0,01	46,17	0,61	0,01	4,73
PSOP	5	07/09/2016 - 30/04/2018	Media	681,45	1032,00	7,24	110,00	12,76	38,29	54,37	253,91	1,05	204,20	0,31	0,03	6,37
			Mediana	614,21	933,00	7,26	88,57	12,59	37,66	44,76	266,88	1,30	177,22	0,01	0,01	1,47
PZAH	3*	07/09/2016 - 25/07/2018	Media	1815,54	2799,00	7,59	133,02	17,77	50,58	52,17	335,50	0,64	251,69	0,72	10,76	25,63
			Mediana	1027,72	1642,50	7,57	116,56	4,51	44,40	47,48	205,88	0,16	216,97	1,04	0,01	5,48

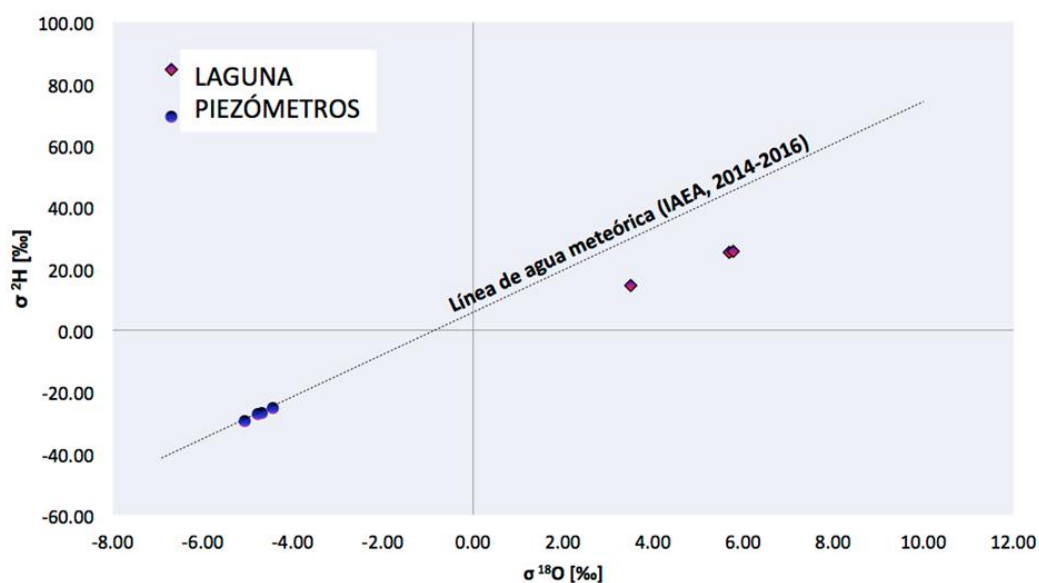


Figura 5. Análisis isotópicos en el agua de la laguna de Santa Olalla (orilla, punto medio y centro de la laguna) y en los cuatro piezómetros instalados en sus orillas. Muestras tomadas el día 04/07/2017. Se ha representado la línea meteórica local (Fuente: www.iaea.org)

Tabla 3. Resultados de la modelización hidroquímica con PHREEQC en las aguas subterráneas y en las aguas superficiales, IS: Índice de saturación.

	FECHAS	IS CALCITA	IS YESO	IS MAGNESITAA	log CO ₂
AGUAS SUBTERRÁNEAS					
PDUL	08/06/2016	-1,81	3,67	-2,53	-20,38
PDUL	15/01/2018	-1,69	4,02	-2,62	-21,07
PSOLW	08/06/2016	-2,81	3,81	-3,63	-20,15
PSOLW	15/01/2018	-1,57	3,52	-2,45	-21,06
PSOLS	25/07/2017	-14,01	45,17	-15	-19,01
PSOLS	15/01/2018	-0,87	3,52	-1,76	-20,27
PSOLE	14/06/2017	-0,88	1,96	-1,61	-20
PSOLE	15/01/2018	-1,01	1,86	-1,78	-20,38
LAGUNAS					
DUL	09/05/2018	0,68	3,17	-0,04	-21,59
DUL	15/01/2018	-0,31	2,26	-1,04	-20,6
SOL	09/05/2018	1,29	3,08	0,57	-21,61
SOL	15/01/2018	1,49	2,44	0,84	-22,46
PAJ	26/01/2017	0,96	1,71	0,45	-21,44

En la Figura 5 se ha representado el resultado de los análisis de isótopos estables del agua (D y O18) tomados en tres puntos de la laguna de Santa Olalla (orilla, punto medio y centro de la laguna) y en los piezómetros (PSOL) de sus orillas N S E y O. También se ha representado la línea meteórica local de isótopos estable en la precipitación desde 2014 a 2016. Se aprecia claramente la marca evaporativa en las aguas de la laguna de Santa Olalla, que es más intensa en el agua del centro de la laguna y menos en la orilla. Por otra parte, las aguas en los cuatro piezómetros muestran una señal isotópica similar a la marca meteórica (i.e. agua de precipitación) lo cual indica una recarga rápida de las aguas de precipitación hacia el acuífero y escaso o nulo fraccionamiento isotópico de las mismas.

En la Tabla 3 se puede observar el resultado de la modelización hidroquímica con PHREEQC en las aguas subterráneas (PDUL, PSOLW, PSOLS y PSOLE) y en las aguas superficiales de las lagunas Dulce-Santa Olalla-Pajas. Se han seleccionado dos muestreos, uno representativo del inicio del periodo estival y otro del invernal. Los resultados indican una sobresaturación de calcita y magnesita en el agua de las lagunas. Por tanto, serán probables los procesos de precipitación de estas especies minerales en los sedimentos lacustres. El yeso está subsaturado en todos los casos. Todas las especies minerales modelizadas están subsaturadas en las aguas subterráneas.

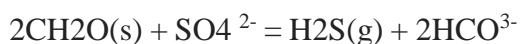
III.2.4. Discusión

Como se comentaba en el apartado anterior, ZAH presenta las aguas menos mineralizadas de todas las lagunas estudiadas (en torno a 600 mg/L de salinidad mediana) y, sin embargo, las aguas subterráneas en su entorno más inmediato son las más mineralizadas (en torno a 1000 mg/L). Por otra parte, es la única laguna en la que el agua subterránea presenta una mayor mineralización que el agua superficial. Es

probable que la razón de este diferente comportamiento esté relacionada con una modificación en el régimen hidrológico en esta laguna, que ha pasado de ser una laguna de descarga en tránsito – como son la mayoría de las lagunas de Doñana – a ser una laguna de recarga (Fernández-Ayuso *et al.* 2018). El vaciado de la laguna se produce, además de por evaporación, mediante recarga hacia la zona saturada. Una fracción del agua - parcialmente evaporada - se infiltra, lo cual aumenta la concentración salina de las aguas subterráneas en el entorno de la laguna. Por otra parte, el agua de la laguna va perdiendo sales progresivamente hacia la zona saturada. Otros autores han puesto recientemente de manifiesto esta alteración, argumentando que el cambio de régimen es debido a la cercanía de los sondeos de extracción de Matalascañas (Dimitriou *et al.* 2017).

Sacks *et al.* (1992) llevaron a cabo un estudio hidrogeoquímico e isotópico y también llevaron a cabo una modelización con WATEQF de los índices de saturación de calcita, sepiolita, yeso y el log. de la PCO₂ en las lagunas DUL, SOL y PAJ en el año 1985 (meses de julio y diciembre) así como en los piezómetros cercanos. Los resultados obtenidos por estos autores, tanto isotópicos como de especiación, son similares a los obtenidos en el presente trabajo, lo cual indica que durante los más de 30 años que han transcurrido entre ambos estudios, los procesos hidrogeoquímicos que están teniendo lugar en el sistema Dulce-Santa Olalla - Pajas no se han modificado sustancialmente. Asimismo, señalan que la precipitación de calcita es un proceso bien documentado en lagunas, debido a una disminución del CO₂ por la actividad fotosintética y el aumento del pH subsiguiente. También documentan una reducción del Mg²⁺ disuelto con respecto a las aguas subterráneas, probablemente por la precipitación de magnesita y quizá sepiolita. Con respecto a la dinámica de los sulfatos, todas las muestras de agua están subsaturadas en yeso, de tal forma que no es

probable una precipitación de esta especie mineral, sino la sulfato-reducción biológica en las aguas subterráneas someras y las aguas superficiales, de acuerdo con la reacción:



Por último, la actividad de las bacterias sulfato reductoras, dependiente de la temperatura (Sacks *et al.* 1992), explicaría que los índices de subsaturación en yeso sean mayores en estiaje.

III.2.5. Conclusiones

Las principales lagunas peridunares situadas en la Reserva Biológica de Doñana poseen aguas salobres de facies fundamentalmente cloruradas sódicas, como corresponde a lagunas someras, la mayoría de ellas estacionales y cercanas a la costa. Las aguas subterráneas en el entorno de las mismas poseen una muy baja mineralización (aguas dulces) en los piezómetros que tienen una profundidad entre 10 – 20 m y una mineralización intermedia (aguas ligeramente salobres) en los piezómetros más someros. En cualquier caso, la salinidad de las aguas subterráneas es menor que la de las aguas superficiales en una proporción que oscila entre 1:20 y 1:7 entre los piezómetros profundos y someros, respectivamente. Esta situación es coherente con el funcionamiento hidrológico de estas lagunas, sistemas alimentados por la precipitación directa y la descarga de aguas subterráneas del acuífero superficial arenoso de los mantos eólicos. En este sentido, se clasifican como lagunas de

descarga en tránsito por la mayoría de los autores. El único sistema que se aleja de este patrón es la laguna de Zahillo, cuyas aguas son las más dulces de las siete que se han estudiado. Por otra parte, la salinidad de estas aguas ha sido, durante el periodo de estudio, menor que la registrada en el agua subterránea en los piezómetros del entorno. Tal situación debe ser debida a una modificación de su funcionamiento hídrico provocada por las extracciones de agua subterránea en la cerca localidad de Matalascañas. Finalmente, las características hidroquímicas y la modelización realizada en las aguas superficiales y subterráneas de la laguna de Santa Olalla no indican que se hayan modificado los procesos hidroquímicos en sus aguas en los últimos 30 años. En cualquier caso, sería recomendable continuar con la monitorización hidrológica en estos sistemas para revertir los impactos detectados y prevenir la degradación en el resto de las lagunas.

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Chapter IV: Time series analysis



IV.1: Unraveling the hydrological behavior of a coastal pond in Doñana National Park (Southwest Spain)

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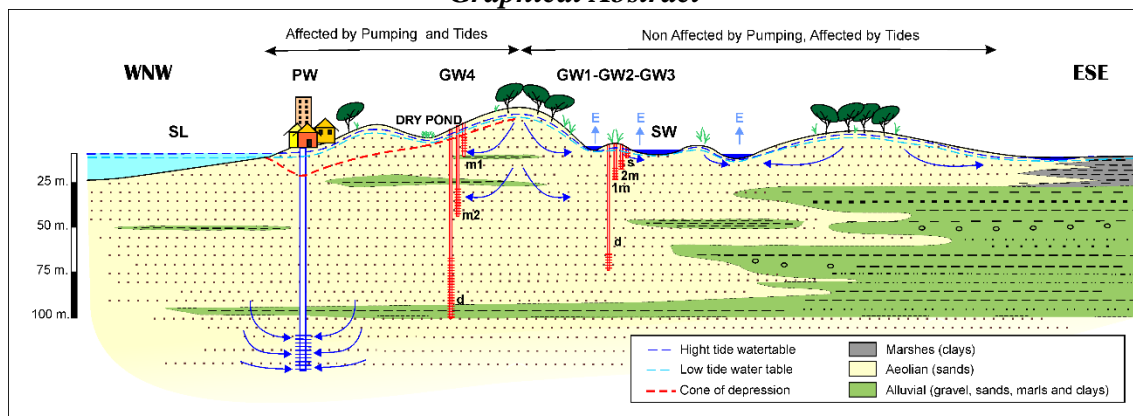
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Graphical Abstract



ABSTRACT

Time series analysis methods have been used to detect behavioral patterns in a set of nine time series. These series contained information in a 3-h time step about meteorological, hydrological and tidal data of a sand dune pond area located in Doñana National Park in the southwest of Spain. The methods used, such as wavelet analysis and additive seasonal decomposition, had never been applied before in the types of ecosystems studied. These approaches have improved the current knowledge of the conceptual model of the Santa Olalla pond system, the only system with a permanent hydroperiod located in this protected area. In addition, complex surface water-groundwater interactions, not visible through descriptive methods, have been distinguished to have a strong seasonal component. Finally, we evaluated the effect of pumping activity in a nearby coastal resort on the water supply of the Santa Olalla pond system. Although direct damage to this sand dune pond has not yet been identified, special attention must be paid in order to maintain groundwater inputs that are integral to maintaining its current status.

IV.1.1. Introduction

Doñana National Park (DNP) is well known for the richness of its ecosystems. It is frequently mentioned that the DNP wetlands are the largest in Western Europe (Dimitriou *et al.* 2017; Green *et al.* 2017). Due to this condition, the Doñana area is protected as a Natural World Heritage Site, Biosphere Reserve and Ramsar Site. Nevertheless, since 1970, several studies have warned about the impact of groundwater withdrawal in the DNP. This withdrawal has stemmed from both crop irrigation (60-90 hm³/year) and the need to satisfy the water demand for urban supply (c. 3 hm³/year) in a touristic coastal resort, Matalascañas (Suso and Llamas, 1993;

Serrano and Serrano 1996; Dimitriou *et al.* 2017). These studies reveal that the maintenance of piezometric levels in the aquifer is at risk. Furthermore, due to the existence of groundwater-dependent ecosystems, the DNP has become a more vulnerable area for the consequences of climate change (Guardiola-Albert and Jackson 2011; Scheffer *et al.* 2015; Green *et al.* 2017). Piezometric levels are generally found at a very shallow depth, and during rainy years more than 3,000 temporary ponds are created in the area. Some of these temporary ponds are located on very permeable aeolian sands which formerly constituted active dunes. Our case study is focused on the Santa Olalla sand dune pond,

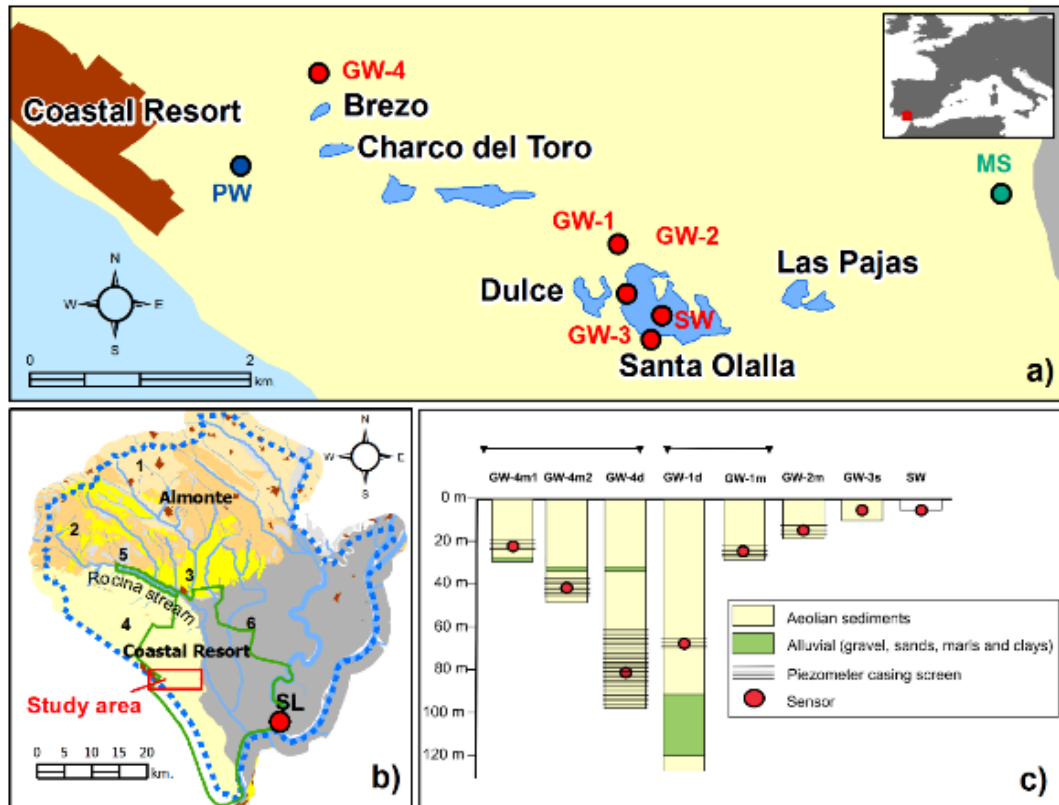


Figure 1. (a) Location of the Santa Olalla pond and monitoring points. GW stands for the measure of groundwater level in a piezometer. SW stands for the measure of surface water level in the pond. PW stands for the measure of groundwater in a pumping well. Blue circles refer to pumping wells, red circles refer to piezometers, and the orange circle refers to SW measurements. Seven sensors for GW measurements are shown. Doñana Meteorological Station (MS) is also shown. (b) Doñana National Park (area inside the green polygon), in the boundaries of the Almonte-Marismas aquifer within the Guadalquivir River Authority Demarcation. Legend for lithology: 1. Calcarenites, Marls, Gypsum and Limestone (Upper Miocene-Pliocene); 2. Sands and Marls (Pliocene); 3. Fossil dunes; 4. Fine sands and coastal dunes; 5. Alluvial (Gravel, Sands, Marls and Clays); 6. Marshes (Quaternary). The tide gauge “Bonanza 2,” where the sea level (SL) is measured, is marked. (c) Lithology and sketches of piezometers used for this study.

the only pond in the DNP with a permanent hydroperiod. Santa Olalla is located 3.7 km away from Matalascañas. This resort uses groundwater from the unconfined unit of the aquifer. This unconfined unit lies within an important recharge area of the aquifer.

Some authors have claimed that intensive groundwater extractions in the coastal resort have caused the drying out of the Brezo and Charco del Toro ponds (Figure 1a), the two closest ponds to the pumping area, just 0.7 km from Matalascañas (Serrano and Serrano 1996; Munoz-Reinoso 2001; Rebollo *et al.* 2008; Serrano and Zunzunegui 2008; Dimitriou *et al.* 2017). Additionally, the hydroperiod and maximum flooded surface area of other ponds have been reduced (Díaz-Paniagua and Aragonés 2015; Dimitriou *et al.* 2017). Due to this situation, some studies have been carried out with the purpose of establishing whether the Santa Olalla pond is being adversely affected in a similar manner (Sacks *et al.* 1992; Lozano *et al.* 2002; Fernández-Ayuso *et al.* 2018). The results of these studies have revealed the complexity of establishing a hydrological conceptual model of Santa Olalla.

Mathematical methods applying time series analysis are increasingly being used to improve the understanding of surface water/groundwater interactions (Kaplan *et al.* 2010; Aguilera *et al.* 2013; Acworth *et al.* 2015; Chiaudani *et al.* 2017; Oh *et al.* 2017; Haaf and Barthel 2018; Trasy *et al.* 2018). Acworth *et al.* (2015) successfully used Fourier analysis on daily and sub-daily scales to identify responses to evapotranspiration in hydraulic head fluctuations. Rebollo *et al.* (2008) applied correlation and spectral analysis to daily time series of surface water and groundwater levels in the sand dune ponds located in the DNP in the period 2001-2007. Their results evidenced the impact of groundwater pumping on the dynamics of the ponds. Four of these monitoring points were the same ones that we have analyzed. Similarly, the time-frequency analysis of rainfall, river level and groundwater level by Chiaudani *et al.* (2017), combined with

hydrogeological knowledge, revealed the conceptual hydrodynamic model of an alluvial aquifer in central Italy.

Time series decomposition is another approach used to characterize hydrological patterns (Machiwal and Jha 2006; Von Asmuth *et al.* 2008; Peterson and Western 2014; Wang *et al.* 2015; Chiaudani *et al.* 2017; Haaf and Barthel 2018). Concerning this method, there is a new flexible additive model developed by Facebook (Prophet) that considers non-periodic changes in trends as well as customizable seasonal periodic components in a Bayesian framework as easily interpretable parameters (Taylor and Letham 2018a). This model's applicability to hydrometeorological data has already been highlighted by some authors such as Papacharalampous *et al.* (2018).

Wavelet analysis for hydrologic time series analysis has been widely applied since the 1990s, with increasing popularity in recent years (Sang 2013). A wavelet transform is able to work with non-stationary time series and detect when significant periods are presented through time (Sleziak *et al.* 2015). One of the applications of wavelet analysis is multi-temporal scale analysis. This method can be applied to hydrologic series to reveal complex hydrological processes and their variability (Torrence and Compo 1998; Labat 2005; Sang 2013). Oh *et al.* (2017) combined dynamic factor analysis with wavelet analysis to identify and quantitatively evaluate complex latent factors controlling groundwater level fluctuations in a riverside alluvial aquifer. These latent factors included the influence of precipitation and direct runoff, seasonal surface water-groundwater interaction, temporal and seasonal agricultural pumping, and regional and local recharge cycles. Therefore, wavelet analysis on fine time scales may reveal relevant information that can characterize surface water-groundwater interactions and hydrogeological functioning of fast response

systems including coastal ponds in sandy environments.

In this paper, sub-daily hydrometeorological time series (i.e., surface water and groundwater levels, precipitation and sea tide series) are characterized on different temporal scales for the period June 2016 to January 2018. The selected methodology is based on three core factors. These factors are the descriptive and quantitative time series analysis, comparison of seasonal components extracted with an additive model (Prophet), and time-frequency wavelet analysis of non-stationary short-term periodicities. The main objectives of the present study are to: (i) apply a new combination of time series analysis methods to detect behavioral patterns in surface and groundwater hydrographs, (ii) update the hydrogeological conceptual model of the Santa Olalla coastal pond system, and (iii) identify the effect of nearby groundwater pumping on the hydrological system.

IV.1.2. Materials and Methods

IV.1.2.1. Study Site

The Donana area (37° N, 6° W) spreads along more than 1000 km² in three provinces of southwestern Spain. This area has a sub-humid Mediterranean climate. Rainfall is distributed on a seasonal basis. Mean precipitation registered in the last 30 years was around 550 mm, most of it taking place during the wet season (October-April). However, interannual variability exists, and during some years the major rainfall occurs in autumn, while in others it occurs in winter or spring (Díaz-Paniagua *et al.* 2015).

The Almonte-Marismas aquifer system (3409 km²) represents the main groundwater resource in the Doñana area. Broadly, Almonte-Marismas is considered as a multilayer alluvial aquifer constituted of silts, sands and gravels of fluvial-deltaic and marine origin (Salvany and Custodio 1995). Santa Olalla and other sand dune ponds are located on unconfined aeolian sands that contain an irregular presence of alluvial clays

and marls. The status of the complete Almonte-Doñana system is classified as “pre-alert” by the latest report of the Guadalquivir River Basin Authority (2018). However, some of the groundwater bodies that constitute the aquifer, including both the coastal area and other areas affected by groundwater pumping for crop irrigation, are in the “alert” category.

The Santa Olalla pond (25 ha) is part of the Dulce-Santa Olalla-Pajas pond system, in which Dulce is a semi-permanent pond, Santa Olalla is a permanent pond and Las Pajas is a seasonal water body. These ponds are located in depressions in the fringe between stabilized and mobile dunes (Figure 1a) and are hydrogeologically connected (Sacks *et al.* 1992). During some extremely rainy years, this system can become connected as a single pond network (Díaz-Paniagua *et al.* 2015). The groundwater flow in the Santa Olalla pond generally moves from the northwest (Dulce area) to the southeast (Pajas area), although some authors have suggested that there are certain differences in the flux direction between the dry and the wet seasons (Sacks *et al.* 1992; Lozano *et al.* 2002). Sacks *et al.* in their study carried out in 1992 based on a solute transport model, stated that in the middle of the wet season (December), the groundwater flux was discharged towards the pond from the southern shore. At the end of the dry season (September), the groundwater flux direction was similar, although groundwater was also discharged from the aquifer through the pond bed as flow patterns were mainly influenced by a deeper flow.

Matalascañas is a coastal resort that belongs to the Almonte municipality, which was built in the 1970s (Figure 1a). Its population of no more than 3,000 inhabitants during the low season increases exponentially during the summer, when it reaches more than 100,000 occupants. In light of this situation, water demand drastically increases from mid-June to the beginning of September. This water demand is solely satisfied by groundwater

Table 1: Characteristics of the monitoring points.

Point	X UTM ETRS89 30N	Y UTM ETRS89 30N	Altitude (m asl)	Depth (m)	Frequency measuremnt (h)	Sensor (brand)
MS	193540	4099220	5	-	3	Baro Diver
SW	190338	4098040	3.4	-	3	Mini Diver CTD
GW-1d	190019	4098532	6.9	72	1	OTT MiniOrpheus
GW-1m	190018	4098535	6.8	30	1	OTT MiniOrpheus
GW-2m	190055	4098288	5.8	17	3	Mini Diver
GW-3s	190336	4097910	5.9	2.7	3	Mini Diver
GW-4m2	187212	4100197	19.5	45	3	OTT Thalímedes
GW4m1	187212	4100197	19.9	22	3	OTT Thalímedes
GW-4d	187208	4100186	20.4	100	3	OTT Mini-Orpheus
PW	183625	4102119	17.4 5	180	1	Level Scout

resources. Its withdrawal comes through five pumping wells bordering the DNP. Some of the wells are used to withdraw water during the whole year, while others only work during the weekends or the summer season. The groundwater abstraction rights are limited to 2.75 hm³/year, although some authors have pointed out that actual consumption is higher (Dimitriou et al. 2017).

IV.1.2.2. Time Series Data

Hourly precipitation data during the period 06/24/2016-01/15/2018 were obtained from the “AlmonteDonana” meteorological station (MS) of the Spanish ~ Meteorological Agency (AEMET). Total rainfall during the hydrological year 2016-2017 was 531 mm, which is similar to the long-term average. Time series of groundwater level (GW) at different monitoring points were obtained from two different sources: data for GW-1 and GW-4 (see Figure 1a) come from the Spanish Geological Survey (IGME), and series from GW-2, GW-3 and PW were collected by Pablo de Olavide University. Specific characteristics of the sensors and time steps are detailed in

Table 1. Data for PW and GW-1d were only available from 05/17/2017 and 02/09/2017, respectively. The PW sensor was installed in a pumping well at 30 m depth.

During the pumping period, the water table drops below the depth of the sensor, so there are no measurements below 5 m asl. Data from GW-4 were used to compare water table levels in piezometers with the same depth as GW-1, but closer to the coastal resort. Santa Olalla pond surface water levels (SW) were recorded with a Diver® water level logger (see Table 1) installed in the deepest area of the pond. On-site measurements from a staff gauge were used to correct the data.

Finally, tidal oscillations (SL) were obtained from the “Bonanza 2” tide gauge station (36.80° N, 6.34° W), which is located 24 km southeast of the Santa Olalla pond, at the mouth of the Guadalquivir River (Figure 1b). This station belongs to the Spanish State Ports Authority.

IV.1.2.3. Methods

The relatively short period analyzed (approximately 1.5 years) does not allow for a robust time series analysis of precipitation data due to its high variability. Therefore, precipitation was only used as Supporting Information. The analysis of hydrological time series characterization was divided into three consecutive steps: (i) visual and

descriptive analysis through time series plots and boxplots; (ii) time series decomposition into relevant periodic seasonal components; (iii) continuous wavelet analysis of high-frequency components in the time-frequency domain. The methods used for the last two steps are described as follows:

(ii) Time series decomposition: distinction of the seasonal (periodic) components of the time series was performed with the Prophet model (Taylor and Letham 2018a). If $y(t)$ is the observed time series, Prophet uses an additive model, where linear growth trends ($g(t)$) are fitted with periodic seasonalities ($s(t)$), plus a normal random error term ($\varepsilon(t)$):

$$y(t) = g(t) + s(t) + \varepsilon(t) \quad (1)$$

We used the implementation of Prophet in the R package *Prophet* (Taylor and Letham 2018b). *Prophet* models linear growth using a simple piecewise constant function. S changepoints at times sj , $j = 1, \dots, S$ (dates where the growth rate is allowed to change) are modeled using a vector of rate adjustments $\delta \in \mathbb{R}^S$, where δ_j is the change in rate at time sj . Prophet puts a sparse prior $\delta_j \sim \text{Laplace}(0, \tau)$ on the magnitudes of the rate changes. The parameter τ controls the flexibility of the model to choose potential changepoints at which the rate is likely to change. Large values will make the trend more flexible and will allow many changepoints. By default, Prophet specifies 25 potential changepoints which are uniformly placed in the first 80% of the time series. After some trials with different

values, we found this setup to be suitable to represent the relatively regular hydrological time series.

Seasonal components are fitted using a partial Fourier sum on the corresponding periodicity (e.g., 365.25 days for yearly component, 7 days for weekly component, etc.) with coefficients estimated from a normal smoothing prior distribution $\beta \sim N(0, \sigma^2)$. The number of cosine-sine terms in the partial sum determines how quickly the seasonality can change, and the smoothing prior parameter (σ^2) controls the strength of the seasonal component. We considered daily, weekly and yearly components for each series.

The *Prophet* developers set default values for the parameters that are appropriate for most forecasting problems (Taylor and Letham 2018a): $\tau = 0.05$, $\sigma^2 = 10$, 10 Fourier terms for the yearly periodic component, three Fourier terms for weekly periodic component and four Fourier terms for daily periodic component. These values proved to be suitable for our data.

(iii) Wavelet analysis: time-frequency analysis was performed through continuous wavelet analysis using the R package WaveletComp (Roesch and Schmidbauer 2018). For a detailed discussion on wavelet analysis, reference is made to Torrence and Compo (1998) and Labat (2005). WaveletComp analyzes the frequency structure of univariate and bivariate time series using the complex-valued Morlet wavelet transform:

$$\varphi(t) = \pi^{-1/4} e^{i\omega t} e^{-t^2/2} \quad (2)$$

where $\psi(t)$ is the mother Morlet wavelet function, t is time and ω is the angular frequency, which is set to 6 rad t^{-1} . This wavelet is widely used for hydrometeorological data (Andreo *et al.* 2006; Fengqi and Lijuan 2015; Schulte *et al.* 2016). It leads to a continuous, complex-valued wavelet transform of the time series,

IV. Time series analysis

and is therefore an information-preserving tool that can be applied to select any time and frequency resolution parameters. The transform can be separated into its real part and its imaginary part, thus providing information on both local amplitude and the instantaneous phase of any periodic process across time. The Morlet wavelet transform of a time series y_t is defined as the convolution of the time series, with versions of the mother wavelet translated in time by h and scaled in frequency by m using a fast Fourier transform:

$$Wave(h, m) = \sum_t y_t \frac{1}{\sqrt{m}} \varphi^*\left(\frac{t-h}{m}\right) \quad (3)$$

The symbol “*” denotes the complex conjugate. The square of the modulus of the wavelet transform can be interpreted as time-frequency (or time-period) wavelet energy density, and is called the wavelet power spectrum:

$$Power(h, m) = \frac{1}{s} |Wave(h, m)|^2 \quad (4)$$

The proportionality factor $\frac{1}{m}$, introduced by Liu *et al.* (2007), is used to reduce bias in high-frequency phenomena. In the *WaveletComp* package, the wavelet power spectrum is visualized with an image plot in the time-period domain. For the purpose of testing the null hypothesis of “no periodicity,” the significance is assessed against a white noise process fitted to the data (Roesch and Schmidbauer 2018). In order to analyze non-stationary periodic components of the series in the time-frequency domain, and complement the previous analysis of seasonal components, continuous wavelet analysis was performed on the differenced data (i.e. $x_t - x_{t-1}$, $t = 2, \dots, n$), where n is the length of the series. This allows comparison of water level lags among monitoring points, and the ability to focus on the higher-frequency components of the series.

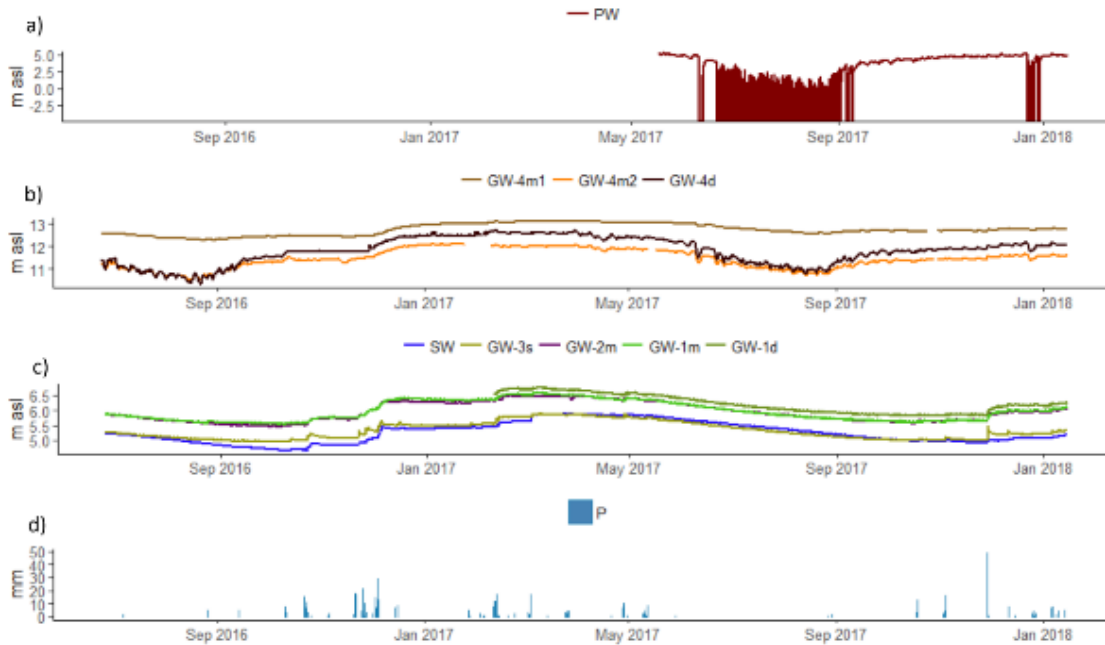


Figure 2: a) Water table evolution in PW. b) Water table evolution in GW-4m2, GW-4m1 and GW-4d. c) Water level evolution in Santa Olalla pond (SW) and water table evolution in four piezometers (GW-2m, GW-3s, GW-1d and GW-1m) located close to the pond. d) Precipitation (P) events during the study period. Sensor locations are shown in Figure 1.

IV.1.3. Results and Discussion

IV.1.3.1. Descriptive Analysis

The nine hydrological time series shown in Figure 2a-2c are strongly influenced by the seasonality effect. A summary of the statistics in the dataset can be seen in Table 2. All the water tables and water levels decreased during the summer, when very few precipitation events occurred. However, at the end of June, even sharper water table drops occurred in the deepest piezometers close to the resort (i.e., GW-4 m2 and GW-4d). Figure 2a shows the time series of the sensor observed in PW (Figure 1a). Pumping effects are clear in GW-4 piezometers (e.g., 1 m of water table

depletion in GW-4d sensor in June 2017). A 2-week window of PW and GW4d time series from 10/13/2017 to 10/30/2017 is shown in Figure 3. The maximum piezometric levels were reached at the end of the weekdays, while at the beginning of the weekend, the groundwater level decreased by up to 30 cm. A time lag between the pumping and the effect on the GW-4d levels can also be seen.

Precipitation events in October 2016 and November 2017 represented the end of the decreasing water level trends of the summer. The range of GW-4 sensors during the year was around 2 m (Table 2).

Table 2: Summary Statistics for Each of the Time Series: SW, Surface Water Levels; GW, Groundwater Levels; PW, Pumping Well; SL, Sea Level.

	Mean	Median	SD	Max	Min	Range
SW	5.26	5.19	0.36	5.89	4.66	1.23
GW-2m	5.95	5.89	0.33	6.48	5.46	1.02
GW-3s	5.32	5.23	0.30	5.90	4.95	0.95
GW-1d	6.23	6.18	0.34	6.78	5.81	0.97
GW-1m	6.03	5.99	0.34	6.60	5.54	1.06
GW-4m2	11.49	11.45	0.45	12.12	10.46	1.66
GW-4m1	12.78	12.75	0.31	13.13	12.26	0.87
GW-4d	11.89	11.91	0.59	12.75	10.29	2.46
PW	1.94	4.20	4.25	5.29	-11.23	16.52
P	0.17	0.00	1.51	48.80	0.00	48.80
SL	1.76	1.72	0.71	3.46	0.31	3.15

This variation is caused by a growth in the volume of tourists in the coastal resort that creates an increase in the water demand. The water level in the pond (SW) was below the water table in the surrounding area during almost the complete study period (Figure 2c). Nonetheless, during the dry season of 2017 (March-October), SW was above the shallow groundwater table near the pond (i.e., GW-3 s). The fact that this circumstance only occurs in certain years illustrates the complexity of the hydrological functioning in the Santa

Olalla pond. Lozano *et al.* (2002), through hydrogeochemical

and isotopic analyses, also detected recharge from the pond to the aquifer on the southern side of the shore in May 2000. Analogous complexity between groundwater and interdunal wetlands was studied by Doss (1993) and Winter (1999) in dune terrain settings located in Indiana and Nebraska. In such studies, Doss and Winter detected how some water bodies changed from flow-through to groundwater recharge. These changes were caused by the interchange of recharge and evapotranspiration in the perimeter of the wetlands.

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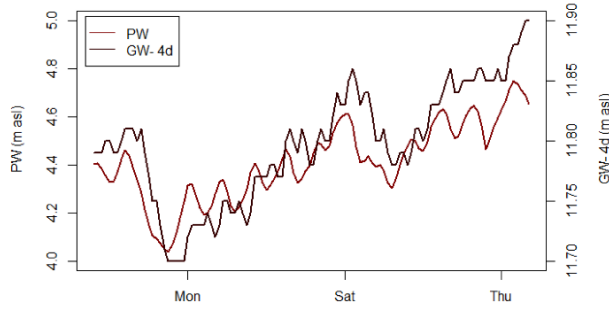


Figure 3: Time series in PW and GW-4d sensors during the time period 10/13/2017-10/26/2017. Water table evolution in the deep and medium-depth piezometers, located in the northwestern part of the pond (i.e. GW-2 m, GW-1 m and GW-1d), showed analogous behavior. GW-2 m, however, had an overflow. In

The boxplots of the distribution of water levels by month in Figure 4 show a similar variation in SW and the shallow level of

from July to October (months 7 to 10) due to evaporation. However, in November and December, distributions were similar again.

The monthly distribution of groundwater levels at medium depths in the northwestern part of the pond (i.e., GW-2 m and GW-1 m) is similar. GW-1d shows smaller variations, likely due to the buffer effect of the regional flux at deeper levels. However, these observations should be interpreted carefully as this point has less than a year of available data (February 2017 to January 2018).

The deeper piezometers GW-4 m2 and GW-4d near the coastal resort show wide yearly variations, and a sharp decrease in the water tables starting in June (month 6 in Figure 4) triggered by the intensification of pumping activity. Groundwater levels then recovered in fall and winter, due

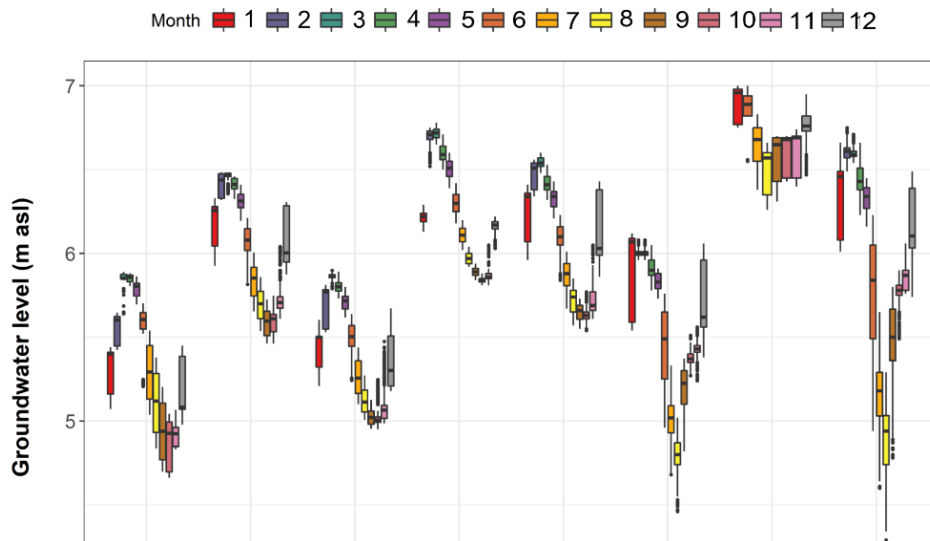


Figure 4: Boxplot diagrams of the monthly distribution of water levels in the Santa Olalla pond (SW) and in the groundwater (GW) monitoring points arranged by distance to the pond. Groundwater levels in GW4 piezometers have been rescaled by subtracting 6 units from the actual measurements. Month 1 corresponds to January, 2 to February, etc.

GW-3 s from January to June (months 1 to 6). There was increased variability in SW compared to GW-3 s

to greater precipitation in December and January. The

Table 3: Squared R and RMSE fit of the time series analyzed with Prophet.

	SW	GW-2m	GW-3s	GW-1d	GW-1m	GW4-m2	GW4-m1	GW-4d
R²	0.996	0.803	0.891	0.627	0.752	0.987	0.997	0.985
RMSE	0.022	0.022	0.141	0.847	0.736	0.045	0.013	0.068

shallowest point near the resort GW-4 m1 shows an almost constant distribution of groundwater levels across the year (only a slight decrease in the summer). Apparently, this piezometer is not affected by pumping activity. This would be due to the presence of fine alluvial materials of low permeability in the first 22 m below the surface and also because groundwater in the resort is pumped at greater depth (Figure 1).

The Prophet additive model performed well for both SW and GW level time series in terms of goodness-of-fit and error measurements (Table 3). Most models show values of R^2 higher than 0.8 and an RMSE lower than 0.1 m asl. GW-1 points show the worst performance, but the representation still captures the main time series patterns. The fit plots in Figure 5 and in the Appendix S1 reflect the adaptability of Prophet to different time series patterns. The oscillations in the fit line in GW-4 m2 reveal the strong weekly periodic component (Figure 5b).

IV.1.3.2. Additive Decomposition

IV.1.3.2.1. Yearly Component

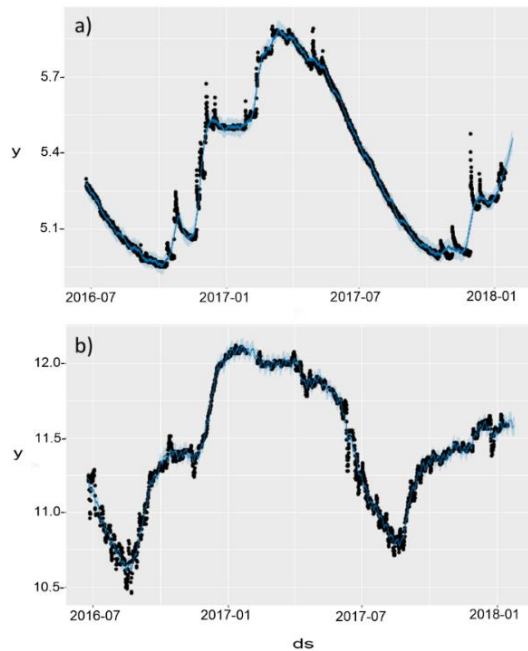


Figure 5: Time series reconstructed by Prophet (blue line) for GW-3 s (a) and GW-4 m2 points (b). Black points are actual measurements.

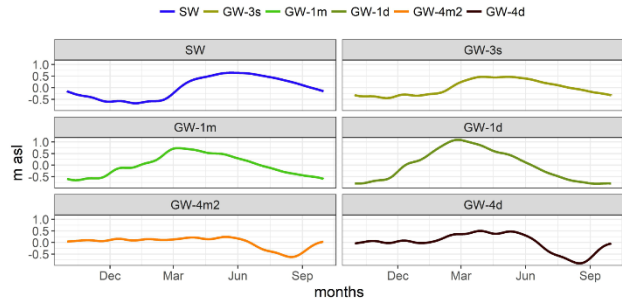


Figure 6: Yearly component of the additive model in SW, GW-3s, GW-1m, GW-1d, GW-4m2 and GW-4d time series

Despite the fact that the hydrological time series are shorter than 2 years, the yearly component allows for clear visualization and comparison of the different patterns the data (Figure 6). Moreover, the plots support the applicability of Prophet to analyze interannual seasonal patterns from a methodological point of view. There are

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similar groundwater level yearly patterns in all points near the pond and in the water level of the pond itself (i.e., SW, GW-1 m, GW-1d, and GW-3 s). The yearly component in the deeper GW-4 points shows a sharp drawdown in the summer, accounting for the pumping influence.

IV.1.3.2.2. Weekly Component

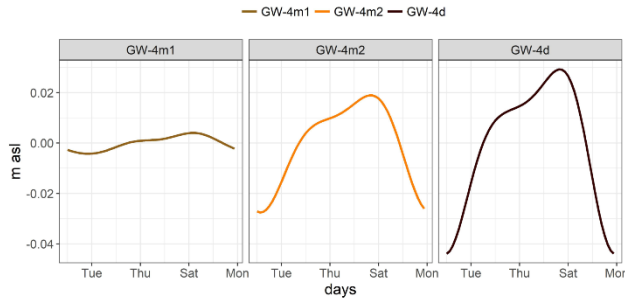


Figure 7: Weekly component of the additive model in GW-4 water table time

Figure 7 shows the weekly component of groundwater levels in GW-4 piezometers. They were the only ones having a significant weekly pattern. In the deepest piezometers (GW-4d and GW-4 m2), weekly variation ranges were found to be an order of magnitude higher than in the shallower GW-4 m1 (0.02 vs. 0.0025 m). This data illustrates the greater effect of the weekly component in the deepest piezometers. A decreasing tendency in piezometric levels can be observed during the weekend when the influx of people at the coastal resort increases (Figure 3). The piezometric levels then recover during the weekdays. These conclusions corroborate the findings of Rebollo *et al.* (2008).

IV.1.3.2.3. Daily Component

The amplitude of the daily components in the pond (SW) and the shallow groundwater levels closest to the pond (GW-3 s) exhibit the evaporation processes most common to the pond itself (Figure 8). The bimodal daily pattern in GW-1 m could be attributed to the tidal effect as will be

discussed in the next section. In the case of GW-2 m, the tidal variations are not so clear. In GW4, an alteration of the tidal signal can be seen, which could be produced by the different time offset expected between groundwater pumping and low and high tidal signals. Furthermore, most of the possible absorption of the tidal signal occurs during the night, when the water withdrawal intensity is higher.

IV.1.3.3. Wavelet Analysis

The wavelet power spectrum and time-averaged power spectrum of the differenced

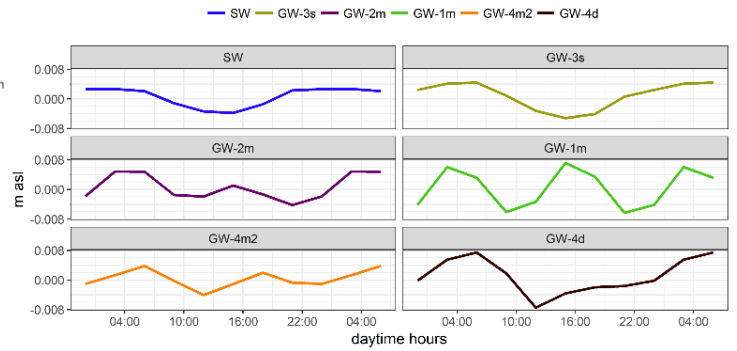


Figure 8: Daily component of the additive model in SW, GW-3s, GW-2m, GW-1m, GW-4m2 and GW-4d time series

univariate series in Figure 9a and 9b show significant daily periodicity in the pond (SW) and in shallow groundwater close to the pond (GW-3 s) due to evaporation processes. The daily component was particularly strong during the summer and dissipated in both autumn 2016 and winter 2017, as shown by the gaps with non-significant areas (no red) and the low power levels in the wavelet spectrums of SW and GW-3 s (Figure 9a and Appendix S2).

On the other hand, all the wavelet power in the medium groundwater levels located in the northwestern part of the pond (GW-1 m and GW-2 m) was concentrated on the semidiurnal periodic component during the whole period studied. This is shown by both the significant red power levels and the black line depicting the ridge of the maximum power levels around the 0.5-day period in Figure 9c. Furthermore, the semidiurnal

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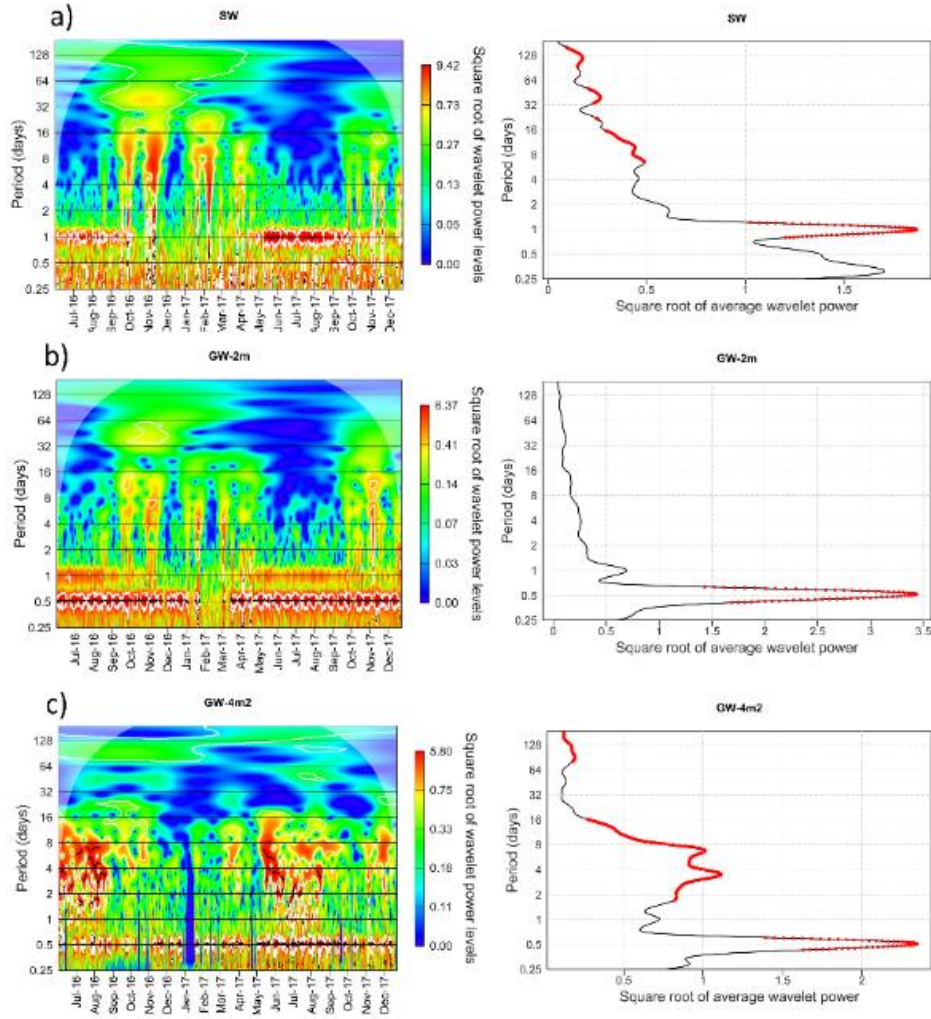


Figure 9: Wavelet power spectrum and wavelet power averages of surface water level in Santa Olalla pond (SW), and in groundwater levels in GW monitoring points (see Figure 1). The power levels in the spectrum are the square root of actual power values in order to accentuate the contrast of the image. In the image plots of wavelet power spectrum, the color scale represents the quantiles of the distribution of wavelet power levels; the area within the white lines represents high power at the 0.1 significance level with respect to the null hypothesis of white noise processes; black lines depict power ridges (maximum levels). In the plots of wavelet power averages, the red dots represent periods where the average of the wavelet power spectrum is significant at the 0.05 level.

periodicity of these series had the highest average power levels of all the points. Similarly, as inferred from the component analysis, these results depict tidal oscillations as the main controlling factor of piezometric variations at these points. The amplitude of the semidiurnal tides in this area of the Atlantic Ocean is relatively constant at approximately 2.5 m. These types of tides are characterized by high tides and low tides alternating every 12.5 h (Appendix S2). There are a couple of small gaps in the dataset between May and July 2017. The

semidiurnal control on GW-2 m (Figure 9c), however, is seen more clearly than it was through the daily component (Figure 8). The gap in semidiurnal periodicity in GW-2 m during February and March 2017 is attributed to the interference caused by the water outflow through the piezometer. Wavelet power spectrums for GW-1d and GW-1 m are not shown because they are very similar to that of GW-2 m. Therefore, homogeneous hydrodynamic behavior in depth can be inferred in the area where these piezometers are located (Figures 1 and 9).

The behavior of GW-4 piezometers, located near the tourist area, is a function of depth and lithology. The deeper GW-4 m2 and GW-4d show relatively constant semidiurnal periodicity which is linked to tidal oscillations and weekly and half-weekly (i.e., weekend) components during the summer related to pumping activity (Figure 9c). GW-4d has almost identical patterns of time-frequency variation, and the plots have been omitted. The average wavelet power of the shallower GW-4 m1 shows the same components, but they are weaker in terms of power levels and irregularly distributed in time. This irregularly distributed time is as if there was a dampened response to the dynamics at the deeper aquifer levels (Figure 9c). At the same time, the average power plots in Figure 9c indicate a slight seasonal effect at periods longer than 1 month that decreases in depth from GW-4 m1 towards GW-4 m2. This would be related to the slower recharge processes through finer, less permeable materials (Figure 1c) and to the groundwater flow through a higher-scale regional flux system, registered by the deeper sensors GW-4 m2 and GW-4d. Overall, the disturbed time-frequency spectrum at GW-4 m2 results from the combined effect of surface hydrometeorological processes and influencing dynamics from the deeper levels. Here, the strength of wavelet analysis for hydrogeological characterization that cannot be unraveled solely through hydrograph inspection and descriptive statistics is evidenced. These manifested differences detected between GW-4 piezometers and piezometers in the Santa Olalla area show that the unconfined aquifer near Santa Olalla is not affected by pumping activity in the coastal resort.

All water level monitoring points, except for the pumping-influenced deeper levels in GW-4, show higher wavelet power in periodicities up to 2 weeks, coinciding with rainfall events which occurred in October and November 2016 (Figure 2). These are the red/orange areas in Figure 9a

and 9b, which are not seen in Figure 9c. These findings show quantitative evidence of relatively fast groundwater responses in the system, as argued by other authors (Sacks *et al.* 1992; Lozano *et al.* 2002).

IV.1.3.4. Enhancement of the Conceptual Model of the Santa Olalla Pond

The results provide new insights into the conceptual hydrogeological model of the Santa Olalla pond. The main findings in the hydrogeological time series analysis are as follows:

- (i) Surface water in the pond (SW) and shallow aquifer (GW-3 s) showed similar behavior (Figures 6–8), including a significant daily periodic oscillation during late spring and summer (Figure 9a and 9b);
- (ii) groundwater in the area surrounding the pond (GW-2 m, GW1 m, and GW-1d) at medium and deep locations (17 to 72 m) had similar seasonal components (Figure 6) and a constant semidiurnal periodicity linked to tidal oscillations (Appendix S2);
- (iii) medium to deep aquifer levels (45 to 100 m) in the vicinity of Matalascañas coastal resort (GW-4 m2 and GW-4d) showed weekly oscillations during the summer due to both groundwater pumping and semidiurnal tidal effects (Figures 7 and 9). The increased specificity found at a sub-daily time step for the effect of groundwater pumping at these points is an improvement from the study carried out by Rebollo *et al.* (2008). The GW-4 m1 piezometer is less affected by groundwater pumping due to the presence of fine materials in this location, which buffers the area, protecting it from the effects of the pumps.

- Groundwater pumping in Matalascañas does not seem to affect groundwater dynamics in the area surrounding the Santa Olalla pond. These results support the current conceptual hydrogeological flux model of the aquifer in Doñana. Due to the fact that the Santa Olalla

pond ~ is located in an area where deep groundwater fluxes discharge, it has water throughout the year (Sacks *et al.* 1992; Lozano *et al.* 2002; Díaz-Paniagua and Aragonés 2015). The primary output from the pond ~ is through evaporation processes. Furthermore, it has been verified that during dry seasons, Santa Olalla may recharge water to the aquifer through the southern shore (GW-3 s).

IV.1.4. Conclusions

Nine hydrometeorological time series from groundwater levels, surface water level, rainfall and sea tides in the Santa Olalla permanent pond area within the DNP have been analyzed. The main contribution of the methodological approach through time series decomposition and wavelet analysis is the disaggregation of overlapping hydrodynamic effects (e.g., evaporation, tides, recharge, pumping, etc.) that cannot be separated by visual inspection of hydrographs and descriptive statistics. Moreover, continuous wavelet analysis allowed for a more concise estimation of dominant temporal scales in the hydrogeological system and assessment of the differences between dry and wet conditions. Shallow groundwater level oscillations in the aquifer near the pond influence the surface water level oscillations in the Santa Olalla pond. Sea tides influence groundwater levels in all medium and deep piezometers. Lastly, a pumping impact has been detected in piezometers close to the coastal resort, but not in the Santa Olalla area. The connection of the Santa Olalla pond with both deep groundwater flux and local flux has been distinguished. In light of the results, it must be highlighted that, although hydrological effects caused by pumping have not yet been identified in the Santa Olalla pond area, in order to guarantee its preservation, special care must be taken to maintain groundwater levels in the Almonte-Marismas aquifer. The outcomes and methods presented in this case study can improve the current knowledge of the

processes occurring in surface water-groundwater interactions in similar contexts.

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Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article. Supporting Information is generally not peer reviewed.

Appendix S1. Fit of the Prophet model in all the time series analyzed. The blue line is the time series reconstructed by Prophet. The black points represent actual measurements.

Appendix S2. Wavelet power spectrum and wavelet power averages of groundwater level GW-3 s and tidal oscillations SL (see Figure 1). The power levels in the spectrum are the square root of actual power values in order to accentuate the contrast of the image. In the image plots of wavelet power spectrum, the color scale represents the quantiles of the distribution of wavelet power

levels; the area within the white lines represents high power at the 0.1 significance level with respect to the null hypothesis of white noise processes; black lines depict power ridges (maximum levels). In the plots of wavelet power averages, the red dots represent periods where the average of the wavelet power spectrum is significant at the 0.05 level.

CHAPTER V: CONCLUSIONS



Conclusions

The main aim of this work has been to improve the knowledge of the surface water-groundwater interactions of the main sand-dune ponds located in Doñana National Park. Throughout this study, the hydrological functioning of these ponds has been greatly improved by hydrodynamics methods, such as water balances, thermal methods and time series analysis that comprises additive methods and wavelet analysis. Furthermore, the previous conceptual model of the Santa Olalla pond has been reviewed and a new one has been proposed for the rest of the ponds. Most of the data used in this thesis were recorded at an hourly scale, thus the detailed time scale is a remarkable aspect of this study.

The specific objectives cited in the Objectives section have been successfully addressed:

- (SO1) In the Santa Olalla pond (part of the Dulce-Santa Olalla-Pajas system), the study of physical and chemical parameters in a wide range of sampling points during various periods has highlighted the complex hydrological behavior of this permanent pond. In addition, oxygen-18 and deuterium analysis of water samples collected in Santa Olalla pond area evinced that groundwater had a similar isotopic signal to the local meteoric water line, implying a fast recharge of the rainfall in the aquifer. Moreover, the isotopic analysis of surface water revealed that the evaporative signal was more intense in the centre of the pond than at the shore, where the local water discharges. The positive gradient of Electrical Conductivity (of more than 6 mS/cm) measured in transects from the shore to the centre of the pond reinforce this explanation. A pH gradient in Santa Olalla and Dulce ponds was also detected from the shore to the centre of the pond, which demonstrates the importance of biological

processes, such as the dissolved CO₂ capture by phytoplankton.

On the one hand, a thermal model carried out with vertical temperature profiles at the centre of the pond indicates that although there is a net groundwater discharge (0.05 hm³/year) during the dry season, slight recharge processes could take place. On the other hand, during the wet season (high water levels) there is a net groundwater discharge of an order of magnitude higher (0.36 hm³/year) and the recharge processes were not detected. These results are consistent with those obtained for the water balance of this pond in 2017 (0.40 hm³/year).

Concerning the time series analysis in Santa Olalla pond area, it has been demonstrated that surface water and shallow groundwater (2.7 m) have a similar hydrodynamic functioning in which the evapotranspiration is the main controlling process in the water levels. Medium and deep groundwater (17-72 m) follow a similar pattern, linked to rainfall seasonality and in which the semidiurnal tidal oscillations can be identified. Wavelet analysis has revealed the existence of both the regional and the local groundwater flux in this pond, which play a crucial role in order to maintain the pond flooded throughout the year. This unique situation could explain why the Santa Olalla pond is the only pond studied that has no seasonal hydroperiod. Its low altitude and its key geographical location in an area where the hydraulic gradients are high, would explain why the regional groundwater discharges in this pond. The semidiurnal tidal signal has been detected at a daily time step in deep groundwater close to the Santa Olalla pond. Information about the sea tides signal in the stabilized dunes has been published for the first time in the framework of this doctoral thesis. However, sea tides only contribute to the hydrological system in terms of compressing and decompressing processes in the aquifer. The tidal signal has not been

detected neither in the surface water nor in the shallow groundwater.

The estimation of saturation indexes in water samples from Dulce, Santa Olalla and Pajas hydrological system and piezometers nearby suggest that there is an oversaturation of calcite. This is as a consequence of CO₂ depletion by algae consumption, and magnesite in the surface water as these minerals are likely to precipitate on the lake sediments. In contrast, gypsum seems to be undersaturated in both the surface water and groundwater samples, which would indicate that sulfate is not originating from this source. Finally, induced sulfate reduction has been detected biologically in the shallow groundwater and surface water. Given the results obtained, similar to those achieved by Sacks *et al.* (1992), it can be stated that the water hydrogeochemistry has not significantly changed in the last 30 years.

- (SO2) Discharge and recharge rates in Santa Olalla, Zahillo and Sopetón ponds during the years 2016-2018 have been estimated by water balances in which the groundwater net flux was the incognita of the equation. Santa Olalla pond has revealed to have a strong dependence on groundwater, as the median value during the study period of groundwater discharge towards the pond was found to be 2.3 mm/day. The same functioning was detected in Sopetón pond, with a median recharge value during the study period of 1.8 mm/day. On the contrary, recharge processes in Zahillo pond were more recurrent than the discharge processes. In this case, surface water infiltrated in the aquifer at a rate of 0.1 mm/day as a median value.

Taking into account the above-mentioned, it has been determined that the conceptual model for these sand-dune ponds is similar in those which still have a natural functioning: there is a high

percentage of water inputs in the pond (three-quarters in Santa Olalla pond and two-thirds in Sopetón pond) from groundwater. The rest of the water inputs are via precipitation. On the other hand, most of the water outputs are via evaporation. This process is responsible for at least 90% of the total surface water outputs. Other water losses from the ponds are due to punctual recharge processes towards the aquifer, after significant rainfall events, or by the existence of outflows towards the marshes, as is the case of Sopetón pond. Thus, these sand-dune ponds are of flow-through type, although discharge processes are dominant in the net balance.

- (SO3) The sand-dune ponds studied (Santa Olalla, Dulce, Pajas, Taraje, Zahillo and Sopetón) have brackish waters (1,500- 8,200 µS/cm) with sodium-chloride facies. Conversely, groundwater from medium-depth (17 m) near the ponds is of freshwater type with low mineralization (187-350 µS/cm), due to the low reactivity of the siliceous sand, and sodium-mixed-chloride facies. Finally, groundwater samples collected from shallow piezometers (3 – 4 m depth) had slight brackish water (690-1,300 µS/cm). These characteristics are in accordance with the hydrological functioning of most of these water bodies as flow-through ponds with a positive net discharge balance and in which the high evaporation causes salts concentration. Some shallow piezometers showed higher E.C. values than the rest during the dry season. Water recharge processes may cause this increment in the salinity of the groundwater. The pH values were alkaline in the surface water and near neutral in the groundwater.

- (SO4) Time series analysis unraveled that piezometers (45-100 m) close to the coastal resort show a weekly pattern related to the fact that more groundwater volume is being withdrawn during the weekends. At a sub-daily scale,

a daily signal was also found for the first time, since groundwater pumping takes place mainly during the night.

This anthropic effect has reached Zahillo pond. The predominant recharge processes in this pond established by the water balances, the significant negative trends obtained in the water table evolution close to this pond, the low pH measured in the surface water in Zahillo pond and its low surface water mineralization reveal that the hydrological regime of this sand-dune pond is altered as a consequence of groundwater pumping in Matalascañas coastal resort. The Brezo and Charco del Toro dried out ponds, located between Zahillo and the coastal resort, suffered from similar modifications in the hydrological functioning and flooded surface before disappearing as ponds.

There is no evidence of the impact of the groundwater pumping in the other studied sand-dune ponds. The results obtained with the hydraulic gradients (there were no hydraulic gradients inversion in Santa Olalla pond area), water balances, additive model Prophet and wavelet analysis reinforced this statement. Even though the conclusions are representative of the hydrological functioning of the ponds during the study period 2015-2018, factors such as climatology or groundwater extractions during other time periods could modify them. Even more if the high response time of the aquifer to these factors is taken into account. Thus, the study of the surface water-groundwater interactions in all of the sand dune-ponds must continue, in order to detect any changes which could indicate damage to the ponds.

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